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Non-linear optics of nano-scale pentacene thin film

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Abstract We have found the new ways to investigate the linear/non-linear optical properties of nanostructure pentacene thin film deposited by thermal evaporation technique. Pentacene is the key material in organic semiconductor technology. The existence of nano-structured thin film was confirmed by atomic force microscopy and X-ray diffraction. The wavelength-dependent transmittance and reflectance were calculated to observe the optical behavior of the pentacene thin film. It has been observed the anomalous dispersion at wavelength $\lambda < 800$ nm, whereas the normal dispersion was found at wavelength $\lambda > 800$. The non-linear refractive index of the deposited films was investigated. The linear optical susceptibility of pentacene thin film was calculated, and we observed the non-linear optical susceptibility of pentacene thin film at about 6×10^{-13} esu. The advantage of this work is to use of spectroscopic method to calculate the liner and non-liner optical response of pentacene thin films rather than expensive Z-scan. The calculated optical behavior of the pentacene thin films could be used in the organic thin films base advanced optoelectronic devices such as telecommunications devices.

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1 Introduction

Non-linear optics is basically the modification of the optical properties of the materials by interaction of light [1, 2]. In non-linear optics, when the optical field is applied on the material, it gives the response in a non-linear manner to the strength of the applied optical field [3]. The refractive index is considered one of the best fundamental basics properties of a material [4]. The refractive index is related to the electronic polarization of the ions and the local field inside the materials. So, the estimation of the refractive indices of any optical material has a great importance in terms of non-linear optics for its applications in optoelectronic devices such as modulators, filters. [5, 6].

Organic materials have an attraction for electric and optical devices. For electric and optical applications, organic thin films [7] required high structural order devices based on small conjugated molecules [8, 9]. Organic semiconductors have advantages over the inorganic semiconductors due to easy fabrication [10], low cost and tunable properties [11]. The optical properties of organic thin films depend on the grain boundaries, traps and imperfections of the film morphology [12].

The pentacene ($C_{22}H_{14}$) consists of five molecules benzene rings. It forms the bulk crystals herringbone structure in which the face of one molecule is close to edge of another [13]. Pentacene having triclinic structure with $a = 7.90$ Å, $b = 6.06$ Å and $c = 16.01$ Å [14]. It is one of the important organic semiconductor materials due to high charge carrier mobility of its solid-state thin films and hence, being used for fabricating of organic thin films for light-emitting diodes, solar cells, lasers and other modern optical devices [15, 16]. The optical and electric properties of pentacene thin films depend on the growth conditions [17, 18]. Four different polymorphs are identified by X-ray diffraction which has different electronic and optical properties [19]. The previous research showed the pentacene as an organic semiconductor for different applications such as optoelectronic devices. However, the non-linear optical property of pentacene thin film has not been investigated completely [20, 21].

The aim of this research work was to study in details linear/non-linear optical properties, structural properties of pentacene thin films for potential use in new emerging areas such as optoelectronics. Spectroscopic method has been employed to determine the linear and non-linear optical properties of pentacene thin films. This method is simpler as compared to Z-scan to calculate the non-linear optics in organic materials.

2 Experimental methods

Pentacene was purchased from Sigma-Aldrich Company without further purification. A proper amount of pentacene was used to charge the molybdenum boat attached with (silica tube crucible) to make high-quality thin film on a highly cleaned glass substrates. The "Edward E-306 A" was used to deposit the pentacene thin films under base pressure 1.5×10^{-5} torr at room temperature. The distance between the source and substrates holder was fixed at 21 cm to avoid the direct heating flow from the source to the substrates. The evaporation rate was fixed at 5 nm/s with maximum thickness 300 nm. The further detail of evaporation can be found in the old published article by Yahia et al. [22].

Structural measurement was taken by X-ray diffraction technique (Shimadzu LabX XRD-6000 with) which has CuK_α as a radiation source of wavelength $\lambda = 1.540598$ Å. The X-ray tube voltage and current were 40 kV and 30 mA, respectively. The 2θ range was 4°–80° with a step size of 0.02 and scanning time of 0.4 s. The UV–Vis–NIR (JASCO-570) double beam spectrophotometer in the range from 190 to 2500 nm was used to find out the absorbance, transmittance and reflectance spectra as a function of wavelengths. All measurements are done on the normal incident of light at room temperature.

The surface roughness and topography and the grain size of the as-deposited pentacene thin film were examined by atomic force microscopy (AFM) [NT-MDT, type Solver Next (Russia)], in non-contact mode. The analysis of the AFM parameters was detected by the attached NT-MDT software.

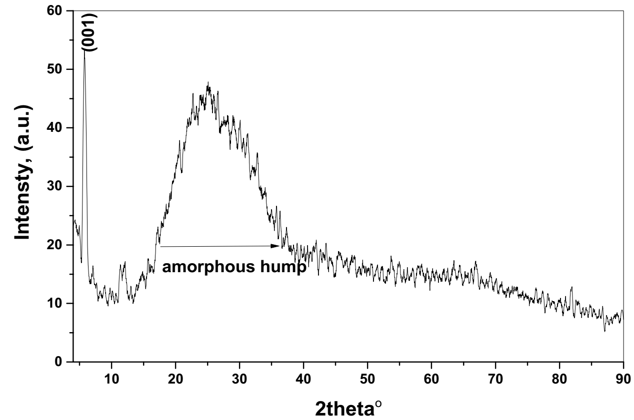

Fig. 1 XRD pattern of pentacene of thickness 300 nm over glass substrates

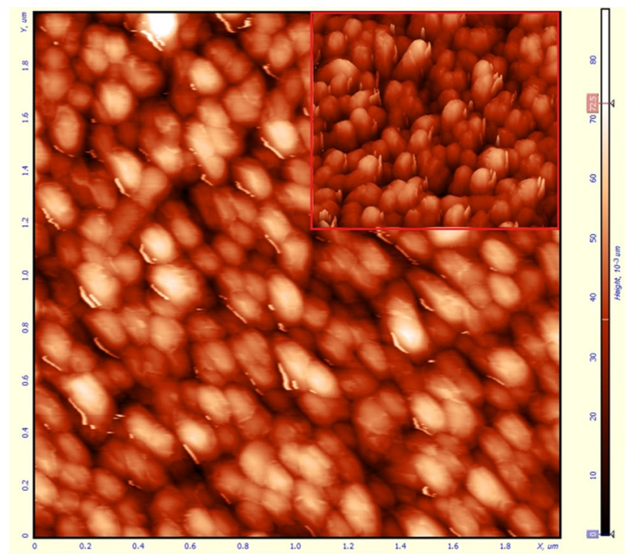

Fig. 2 2D/3D AFM micrographs of pentacene of thickness 300 nm over glass substrates

3 Results and discussion

3.1 Structural analysis

XRD analysis of pentacene thin film is shown in Fig. 1. XRD pattern was recorded at room temperature. XRD data showed a single peak at 6.0651° corresponding to (001) as agreed by JCPD 00-054-2250 which has also been reported by Shin et al. [23] and Minakata et al. [24] for the pentacene thin film. Pentacene has a single preferred orientation of (001) plane superimposed/dipped in a wide scale broad hump characterized the amorphous matrix. Scherrer's formula was used to find out the grain size of the film for (001) plane as follows [25]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \quad (1)$$

In the above equation, λ is the wavelength of X-ray, β is the full width half maximum, and θ is the Bragg's angle of diffraction peak. The grain size of pentacene thin film along (001) plane was found to have 34 nm. Our XRD data also support the formation of nano-scale film. Finally, we can concluded that the as-deposited film showed good crystalline at the orientation (001) plane. This can be compared with previous data obtained by Kim et al. [26].

For surface morphology of pentacene thin films, we have used atomic force microscopy (AFM). Two-dimensional and three-dimensional (2D/3D) AFM image is shown in Fig. 2. Two-dimensional AFM topographies of pentacene thin films revealed the nano-clusters spherical particles, and the grain size are heterogeneous with average values equal 104 nm. Surface roughness has a fundamental role for dielectric, optical properties of pentacene thin films [27]. The surface roughness (*Ra*) was found to be 8 nm.

3.2 Optical properties of nano-pentacene thin films

The spectral distribution of transmittance $T(\lambda)$ and reflectance $R(\lambda)$ of pentacene thin film is shown in Fig. 3. The wavelength range was from 300 to 2500 nm. The average transmittance was noticed above 80 %. To calculate the value of absorption index k from the absorption coefficient following relation used [28]:

$$k = \frac{\alpha\lambda}{4\pi}, \quad (2)$$

where $\alpha = A/t$, A represents the absorbance and t is the thickness of the studied film. The spectral distribution of refractive index (n) and absorption index (k) versus wavelength for the pentacene thin films is shown in Fig. 4. The anomalous dispersion was found at $\lambda < 800$ nm. The normal dispersion was found at $\lambda > 800$. The anomalous behavior is due to the resonance effect that occurs between incident electromagnetic radiation and electrons polarization. This result leads to the coupling of electron in the pentacene films to the oscillating electric filed [29].

3.3 Non-linear optical properties pentacene

Non-linear optical properties of the materials are very important for different applications such as photonic applications [30, 31]. Organic materials are superior then inorganic materials in terms of optical and non-linear optical properties [32, 33]. The induced electrical polarization described the effect of light wave on a material. So, the polarization density is the effect of susceptibility on the light traveling through any medium. Non-linear electron polarizability P_{NL} can be expressed as [34]:

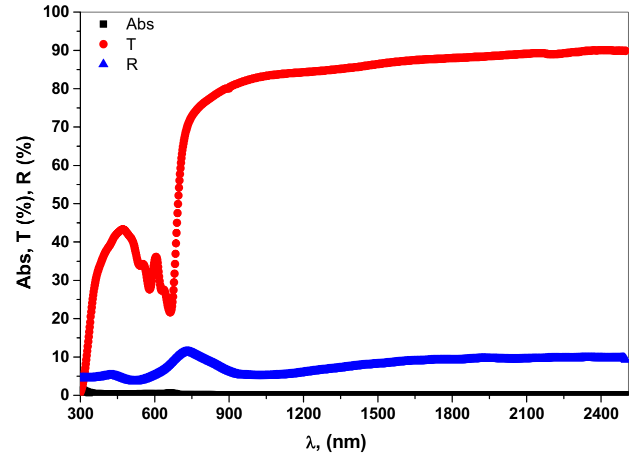

Fig. 3 Transmittance $T(\lambda)$ and reflectance $R(\lambda)$ of pentacene thin film

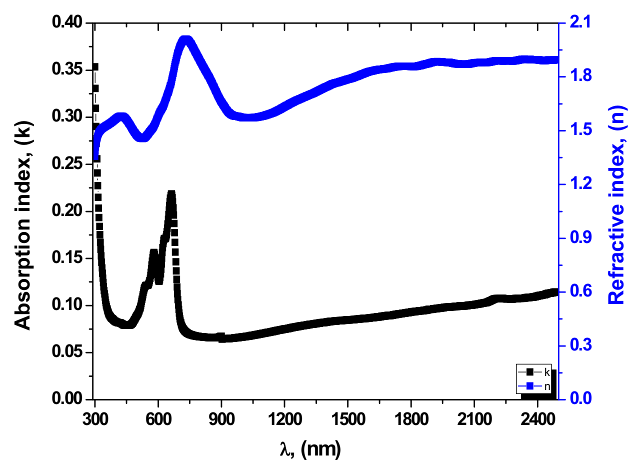

Fig. 4 Absorption index (k) and refractive index (n) of pentacene thin film

$$p = \chi^{(1)}E + P_{NL}, \quad (3)$$

where

$$P_{NL} = \chi^{(2)}E^2 + \chi^{(3)}E^3, \quad (4)$$

where P represents the polarizability, $\chi^{(1)}$ expresses linear optical susceptibility, $\chi^{(2)}$ is known as the second-order non-linear optical susceptibility and $\chi^{(3)}$ showing third-order non-linear optical susceptibility. In case of refractive index, $n(\lambda)$ following equation is used:

$$n(\lambda) = n_0(\lambda) + n_2\left(E^2\right), \quad (5)$$

In Eq. (5), the components of $n(\lambda)$ having the rule: $n_o(\lambda) \gg n_2(\lambda)$, i.e., $n(\lambda) = n_o(\lambda)$ and (E_2) is the mean

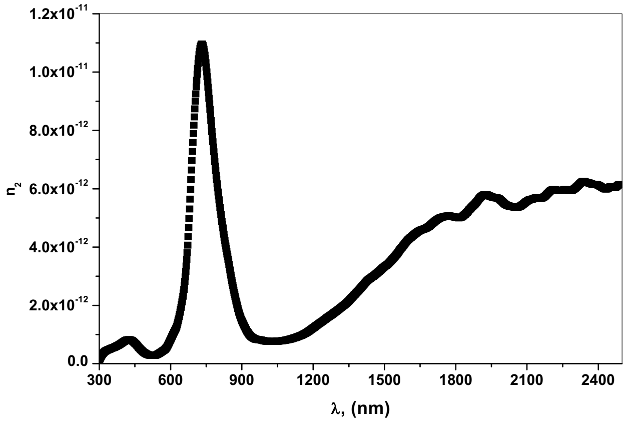

Fig. 5 Non-linear refractive index (n_2) of pentacene thin film

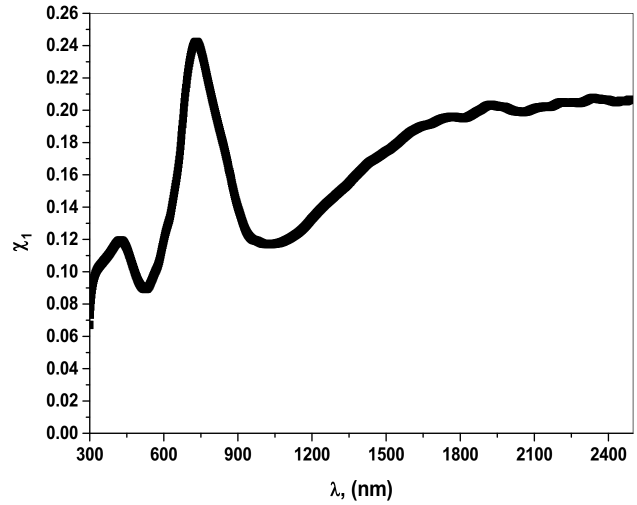

Fig. 6 Linear optical susceptibility (χ_1) of pentacene thin film

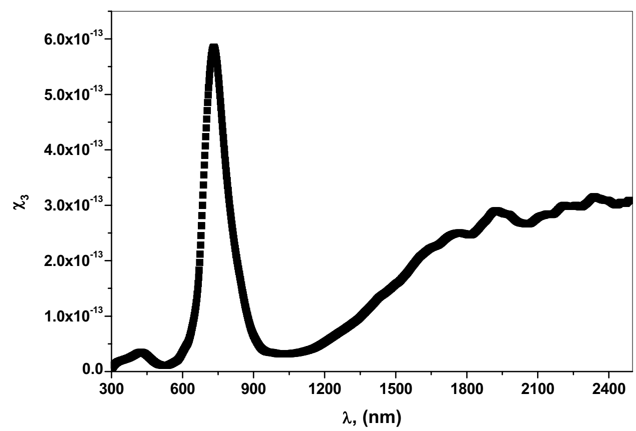

Fig. 7 Non-linear optical susceptibility (χ_3) of pentacene thin film

square of electric field. To represent the linear optical susceptibility $\chi^{(1)}$ of a medium following equation can be used [35]:

$$\chi^{(1)} = \left(n^2 - 1\right)/4\pi, \tag{6}$$

On the basis of linear refractive index $no(\lambda)$, the non-linear optical susceptibility $\chi^{(3)}$ and linear optical susceptibility $\chi^{(1)}$ as under [36]:

$$\chi^{(3)} = A\left(\chi^{(1)}\right)^4, \tag{7}$$

So we can get [37]:

$$\chi^{(3)} = \frac{A}{(4\pi)^4}\left(n_0^2 - 1\right)^4, \tag{8}$$

where A is a constant and equals 1.7×10^{-10}. The non-linear refractive index is also one of the most concern for optical devices in term of non-linear effects. It is the small variation of the refractive index that related to the light intensity. For the expression of non-liner refractive index following relationship is used [38]:

$$n_2 = \frac{12\pi\chi^{(3)}}{n_o}, \tag{9}$$

Calculated non-linear refractive of pentacene thin films is represented in Fig. 5, and the value observed is about 1.12×10^{-11}. The linear optical susceptibility $\chi^{(1)}$ is represented in Fig. 6, and its maximum value equals to 0.25. Figure 7 shows the third-order non-liner optical susceptibility of pentacene thin film. The maximum value of third-order non-linear susceptibility of pentacene was found to be 6×10^{-13} esu. This value is higher as compared to other organic compounds such as naphthalene, anthracene [39]. Such a large electro-optic effect of pentacene is showing the best characteristic of organic–electronic materials, owing to the high polarizability of the extended electron system [40].

4 Conclusion

The AFM and X-ray diffractometry confirm the nanostructure pentacene thin film with the grain size 104 nm and surface roughness 8 nm. The refractive index n and the absorption index k were calculated from the transmittance $T(\lambda)$ and reflectance $R(\lambda)$. These values reflect the wavelength-dependent optical properties of the pentacene thin film. Anomalous dispersion was found at $\lambda < 800$ nm, and normal dispersion was observed at $\lambda > 800$ of the pentacene thin films. The non-linear refractive index was noticed about 1.12×10^{-11}. This article shows the advantages of spectroscopic method over Z-scan to calculate the linear and non-linear optics of organic thin films.

The non-linear optical susceptibility $\chi^{(3)}$ of pentacene thin film was calculated, and it is maximum at 6×10^{-13} esu. This work could be quite useful to observe the linear and non-linear optics of organic thin films for optoelectronic devices.

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