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Impact of annealing on the structural and optical properties of methylene green nanostructure films prepared by drop casting

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ABSTRACT

The methylene green (MG) powder was found to be polycrystalline with the triclinic system. MG films were deposited by drop coating technique. X-ray diffraction and scanning electron microscopy showed that the MG films have nanostructure nature. It is found that the crystal size is increased by annealing. Optical properties of nanostructured MG films were performed in the spectral range from 200 to 2500 nm to determine the optical constants (*n* and *k*). The absorption coefficient of the as-deposited film revealed a two indirect allowed optical band gap with values of 1.90 and 3.11 eV, which increased by annealing to 2 and 3.48 eV, respectively. The dispersion of *n* was discussed in terms of the single oscillator model. The high frequency dielectric constant and the lattice dielectric constant were estimated and found to decreased by annealing.

1. Introduction

It is interesting to search for new materials with promising performance characteristics as well as the improvement in device fabrication. Compounds classified as heterocyclic probably constitute the largest and most varied family of organic compounds Carbocyclic compounds may in principle be converted into a collection of heterocyclic analogy by replacing one or more of the ring carbon atoms with different elements.

The dyes usage in the industries has been increased such as: plastic, textile, dye, dyestuffs, rubber, paper, leather, cosmetics, food, carpet and printing wastewater extensively [1,2]. Methylene green (MG), with its molecular structure depicted in Fig. 1, is a heterocyclic aromatic chemical compound. It is a basic dye used as a chromatin stain, a differential stain for RNA and DNA, and a tracking dye for DNA in electrophoresis [3]. It is used commonly with bright-field microscopes to dye the chromatin of cells so that they are more easily viewed. MG has also been recommended as a suitable dye for the metachromatic demonstration of amyloid [3].

MG has been studied spectrophotometrically, electrochemically and cyclicvoltammetry [4], but physical studies of MG are rare. The study of the optical constants of materials is very interesting for many reasons. Firstly, the use of materials in optical devices requires brief knowledge of their optical constants over a wide range of wavelengths. Secondly, the optical absorption measurements are used to obtain information concerning the band structure of the organic semiconductor thin films. Thus, it is important to reveal the properties of MG as a new semiconductor material for electronic device applications. In this work, we studied the influence of the annealing temperature on the structure and the optical parameters of MG thin films deposited by drop casting technique.

2. Experimental details

2.1. Films preparation

The MG powder was obtained from Fluka Company. Thin films of MG were fabricated using a drop casting technique at room temperature (300 K). A 2 mg of MG powder was dissolved in 25 mL of methyl alcohol. The mixture was magnetically stirred for 5 min for obtaining a homogenous coating solution. Simple, two drops of this solution were dropped onto $2\times2\ cm^2$ optically flat quartz substrates, which were previously cleaned. The whole surface of the substrate was covered by a homogeneous layer of MG film. Film thickness was checked by an interferometric

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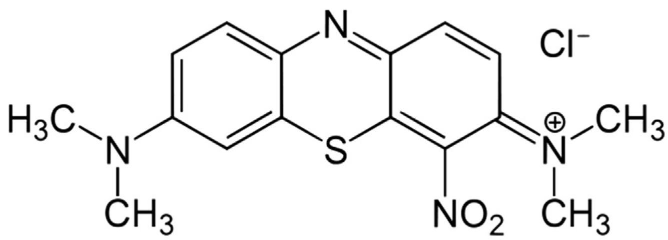

Fig. 1. The molecular structure of MG.

method [5] and found to be 250 nm. For annealing, some samples were thermally heated in air at 453 K for two hours in a compact furnace. Finally, the temperature inside the furnace was left to decrease slowly until reaching the ambient temperature.

2.2. Characterization techniques

The structural characteristics of MG thin films were investigated by X-ray diffraction (XRD) patterns. A Philips X-ray diffractometer (model X' pert) operated at 40 kV and 25 mA was used in the measurements with utilized monochromatic CuK_α radiation. The diffraction patterns were recorded automatically with a scanning speed of 2 degrees per minute. However, the diffraction scan at 0.5 degrees per minute scanning speed was acquired for the individual peaks to determine the crystalline size. The film surface morphology was checked using field emission gun scanning electron microscope (SEM) (Quanta FEG 250).

The transmittance, T, and the reflectance, R, of the films were measured at normal incidence in the spectral range 200–2500 nm using a double-beam spectrophotometer (JASCO, V-570 UV–vis–NIR). The absolute values of transmittance and reflectance were used to determine the optical constants such as refractive index, n, and absorption index, k, by applying a special computer program [6] based on Murmann's exact equations [7]. The experimental errors estimated by using a computational method are given previously [8] and it is found that for film thickness measurements is $\pm 2\%$ and for T and R calculations is $\pm 1\%$, for n it is $\pm 2.5\%$ and for k it is $\pm 2.3\%$.

3. Results and discussion

3.1. Structure characterization

XRD patterns of MG in the powder form were investigated at room temperature (300 K) and the 2θ ranged from 5° to 70°. Fig. 2 presents the XRD patterns for the powder of MG compound; it shows that the powder of MG is polycrystalline structure. The CRYSFIRE computer program [9] indexes all the diffraction lines and calculates the lattice parameters. The analysis indicated that MG has a triclinic crystal system with space group P-1 and the lattice parameters are given as a=1.098 nm, b=1.581 nm, c=1.768 nm, α=62.13°, β=114.43° and γ=70.5°. CHECKCELL program [10] calculates the indicated Miller indices (hkl) for each diffraction peak. The interplanar spacing (d_{hkl}) and the corresponding values of Miller indices $h\ k\ l$ for each diffraction peak are listed in Table 1.

Fig. 3 illustrates the patterns of the as-deposited and annealed MG films. As observed, there is only one significant peak at around 2θ=21° implying a preferential orientation in the (221) direction. This means that the MG films are belonging to the nano-sized structure. Also, the intensity of the peak is slightly increased while its width is decreased with annealing. This indicated that the increase of crystallinity with annealing. The crystal size, L, may be estimated from the half width value of the XRD peak, using the

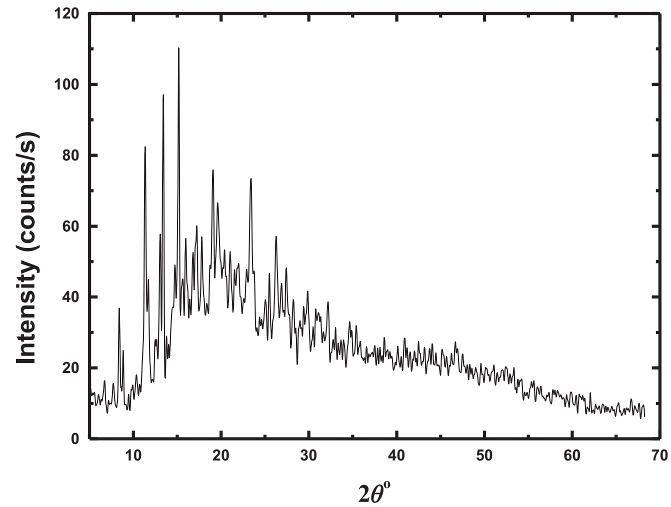

Fig. 2. XRD pattern of MG compound in the powder form.

Table 1
The interplanar spacing (d_{hkl}) and the values of Miller indices $h\ k\ l$ for MG powder.

No.	2θ		d_{hkl} (nm)		I/Io	h	k	l
	Observed	Calculated	Observed	Calculated				
1	7.722	7.742	11.439	11.409	4.74	0	0	1
2	8.399	8.368	10.517	10.558	34.40	0	1	0
3	8.835	8.870	9.999	9.962	19.68	1	1	0
4	11.334	11.277	7.800	7.840	71.12	0	1	2
5	11.647	11.709	7.559	7.552	28.95	1	0	0
6	12.567	12.551	7.038	7.047	9.42	0	2	1
7	13.068	13.095	6.769	6.755	49.56	1	1	1
8	13.408	13.427	6.558	6.589	99.26	−1	1	1
9	15.173	15.160	5.834	5.839	100	−1	1	3
10	15.968	15.964	5.545	5.547	43.14	−1	−1	2
11	17.175	17.163	5.158	5.162	35.01	−1	2	3
12	17.788	17.793	4.989	4.981	58.74	2	2	0
13	19.094	19.071	4.644	4.650	41.99	2	1	0
14	19.636	19.632	4.517	4.518	30.16	1	3	0
15	21.019	21.062	4.222	4.215	25.00	2	2	1
16	21.833	21.806	4.067	4.072	42.87	1	3	3
17	23.383	23.371	3.804	3.803	21.60	0	0	3
18	25.481	25.462	3.492	3.495	32.22	−1	2	5
19	26.277	26.230	3.388	3.395	21.60	−2	1	5
20	–	26.364	–	3.378	–	2	2	2
21	27.421	27.439	3.249	3.248	21.52	1	3	4
22	28.267	28.296	3.154	3.151	13.56	1	5	3
23	29.794	29.759	2.996	3.000	14.55	−3	−4	1
24	32.169	32.144	2.780	2.782	12.68	−3	2	5
25	–	32.248	–	2.774	–	−2	−2	4

Scherrer's equation [11,12].

$$L = \frac{K_s \lambda}{\beta \cos \theta} \qquad (1)$$

where K_s is the Scherrer's constant which has a value of 0.95 [11,12], λ is the X-ray wavelength (λ=0.15406 nm), β is the width of a strong peak in radians at half maximum intensity, and θ is the corresponding Bragg angle. The crystal size of the as-deposited and annealed films was calculated as19.5 nm and 27.69 nm, respectively. It is clear that the crystal size increases by annealing, which indicates that the annealing temperature of MG films results in significant changes in the microstructure of these films.

Fig. 4 shows micrographs of the as-deposited and annealed MG films. The SEM image of the as-deposited films (Fig. 4a) shows clearly almost uniform distribution of grains having size 220–440 nm. The SEM image of the annealed films (Fig. 4b) shows the surface morphology of the annealed film, where the particles are