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Thermal behavior, structure formation and optical characteristics of nanostructured basic fuchsine thin films

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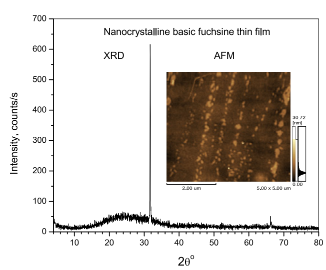
HIGHLIGHTS

- Polycrystalline BF powder becomes nanocrystallites film upon thermal deposition.
- BF has thermal stability up to 265 °C.
- BF can be applied as optical filter material.
- The type of electron transition is indirect allowed with E_g of 1.91 eV.
- Annealing temperatures influenced absorption and dispersion parameters of BF films.

GRAPHICAL ABSTRACT



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ABSTRACT

Thin films of basic fuchsine, BF, are prepared by thermal evaporation technique. The data of thermal gravimetric analysis, TGA, showed that BF has a thermal stability up to the temperature of 265 °C. The structural characteristics of BF thin films are investigated by using X-ray diffraction, and atomic force microscope techniques. BF is polycrystalline in powder form; it becomes nanocrystallites in thin film condition. Annealing temperatures decreased crystallites size and influenced optical constants of BF films. Optical constants of BF films were estimated by using spectrophotometer measurements of transmittance and reflectance in the spectral range from 190 to 2500 nm. The dependence of absorption coefficient on the photon energy and annealing temperatures was determined and the analysis of the results showed that the optical transition in BF films is indirect allowed one. The onset and fundamental energy gap of BF thin films are 1.91 and 3.72 eV, respectively and they decrease by annealing temperatures. The optical dielectric constants and dispersion parameters of BF thin film are calculated and showed remarkable dependence on photon energy and annealing temperatures.

1. Introduction

Organic dyes play an important role as a functional component in electrochemical systems as light harvesters [1], photocatalysts [2] and substrate materials [3]. Theses applications take the advantage of the inherent ability of the dye to absorb light and its electrochemical properties and converts to electricity via photosensitive systems [4–6]. This role is a rapidly expanding field of which dye sensitized solar cells (DSSCs) [7–9]. DSSCs represent great promise as a renewable source of electric energy; they are an interesting as an inexpensive alternative to conventional p–n

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inorganic solar cells. High conversion efficiency, ease of manufacturing and low production costs, makes the DSSCs technology an attractive approach for large-scale solar energy conversion [10].

Most of dyes behave as organic semiconductors; they exhibit a wide range of properties such as photoconductivity, electroluminescence, fluorescence, metallic conductivity, photovoltaic effects and superconductivity [11–13]. The major advantages over inorganic semiconductors are determined by the ability of considerable research interest in view of its great promise for large area, light weight, simple fabrication methods and flexible electronics applications.

Basic fuchsine (BF) is a triaminotriphenylmethane dye with molecular formula $C_{20}H_{20}ClN_3$ and its molecular structure is shown in Fig. 1. It is a mixture of three dyes pararosaniline, rosaniline, and magenta II. This dye is widely used as coloring agent for textile and leather materials, and staining of biological tissues [14]. The electrical study of BF thin films showed that it behaves as a semiconductor and its electrical conductivity is of the order of 10^9–$10^{11}(\Omega\ cm)^{-1}$ [15]. The nonlinear optical response of thermo-optic origin exhibited by a series of fuchsine dyes at low continuous wave laser powers is studied in liquid and solid media and its optical limiter action based on nonlinear refraction is demonstrated [16]. The determination of the fluorescence quantum yield of BF dye in the presence of silver sol is studied using the dual beam thermal lens technique. Silver nanoparticles were prepared by femto second laser ablation. It is observed that the presence of silver sol decreases the fluorescence quantum efficiency due to the non-radiative relaxation of the absorbed energy [17]. Spectral absorption profiles at the UV and visible ranges were recorded spectrophotometrically for solutions of various BFs [18]. The study was performed to detect whether absorption spectra could vary as a function of BF origin up to the point of being suspected of affecting potentially the spectrum of stained chromatin. The results indicate constancy in the spectral absorption characteristics for the absorption profiles at the visible range [18].

Aqueous solution of BF dye is studied spectrophotometrically for possible application in the low-dose food irradiation dosimeters [19]. Absorption spectra of unirradiated and irradiated solutions are determined and the decrease in absorbance with the dose was noted down. Radiation-induced bleaching of the dye was measured at wavelengths of maximum absorption λ_{max} (540 nm) as well as 510 nm and 460 nm. At all these wavelengths, the decrease in absorbance of the dosimeter was linear with respect to the absorbed dose from 50 Gy to 600 Gy [19]. The study on the effect of different light and temperature conditions also showed that the response gradually decreases during the storage period of 34 days, which indicates that BF dye is photosensitive as well as thermally sensitive [19]. Spectroscopic and electrochemical studies of the interaction between BF and DNA were investigated [20]. The visible absorption spectroscopic study shows that the binding mode of BF to DNA is intercalative binding and electrostatic binding when the ratio of the concentration of DNA to BF is smaller than 0.2, and a

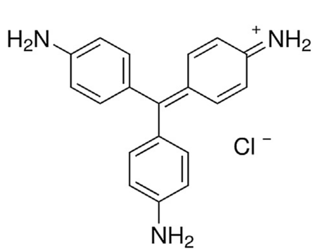

Fig. 1. Molecular structure of basic fuchsine.

new substance, which produces a new absorption peak, is obtained via a covalent binding between DNA and BF apart from intercalative binding and electrostatic binding. Recently, different transition metal complexes are used as a photo catalyst in the photo catalytic degradation of various dyes [21,22]. Potassium hexacyanoferrete (II) was used as semiconductor in photo catalytic degradation of BF [21], while degradation of BF was used as a probe to explore the influencing factors on the photo degradation reaction by $H_4SiW_6O_{40}/SiO_2$ sensitized by H_2O_2 [22].

In designing semiconductor devices, the constituent materials are often provided as thin films. The optical properties of thin films play an important role in determining its electronic structure since it provides useful information to analyze some features concerning its band structure. The optical band gap energy of the semiconductor is an important parameter that plays a major role in the construction of photovoltaic cells. The evaluation of optical dispersions is of considerable importance for applications in integrated optical devices such as switches, filters and modulators. The study of optical properties of thin films has a special significance in the world of technology and industry for the development of new optical devices. However, the optical properties of BF in bulk and thin film conditions are not yet fully clarified. In the present study we investigate the structural and thermal behavior of thermally evaporated BF thin films and we found that BF films became nanocrystallites upon thermal deposition and it is thermally stable up to 265 °C. The dispersion parameters of BF films are determined in anomalous and normal dispersion regions of spectrum by applying multi-oscillator and single oscillator models, respectively. The absorption characteristics of BF films are analyzed within the frame work of band–band electron transition theory.

2. Experimental techniques

BF as a dark green powder was purchased from Sigma–Aldrich Chem. Co. and it was used in as-received condition without any further purification. Thin films of BF were prepared by thermal evaporation technique using a high vacuum coating unit (Edwards E 306 A, England). During the deposition process, the vacuum pressure is about 2×10^{-5} mbar. The films were deposited onto clean optical flat glass and quartz substrates for structural and optical measurements, respectively. These substrates were carefully cleaned by chromic acid for 15 min and then rinsed by deionized water. The powder of BF was sublimated from quartz crucible heated gradually by molybdenum boat shaped filament. The deposition rate and the film thicknesses were measured during the evaporation using a quartz crystal thickness monitor (Model TM-350 MAXTEK, Inc. USA) attached to the coating system. The grown film thickness of BF is 470 nm with deposition rate 0.25 nm/s. A shutter, fixed near to the substrate was used to avoid any probable contamination on the substrates in the initial stage of evaporation process and to control the thickness of films accurately.

Thermal gravimetric analysis (TGA) and derivative of thermal gravimetric (DTG) are measured by using thermogravimetric analyzer (Shimadzu TG-50 Thermo balance, Japan). The measurements were achieved in the temperature range from 30 to 800 °C with a heating rate 10 °C/min. and under nitrogen atmosphere with flow rate 30 ml/min.

The x-ray diffraction measurements are carried out by using a Philips X-ray diffraction system (model X/Pert Pro.) with utilized monochromatic CuK_α radiation of $\lambda = 1.5418$ Å. The system was operated at 40 kV and 30 mA. The 2θ scanning range was from 4 to 80° with step time 1s and step size of $2\theta = 0.1°$.

The morphology of BF films was examined by atomic force microscope (Model: Wet – SPM, Scanning Probe microscope, Shimadzu, Contact mode, made in Japan). The microscope can