Dyes and Pigments 101 (2014) 212–220

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Impact of annealing process on stacking orientations and second order nonlinear optical properties of metallophthalocyanine thin films and nanostructures

A. Zawadzka[a,*], P. Płóciennik[a], J. Strzelecki[a], A. Korcala[a], A.K. Arof[b], B. Sahraoui[c,*]

[a] Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland
[b] Centre for Ionics University of Malaya, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
[c] LUNAM Université, Université d'Angers, CNRS UMR 6200, Laboratoire MOLTECH-Anjou, 2 bd Lavoisier, 49045 Angers Cedex, France

ARTICLE INFO

Article history:
Received 10 July 2013
Received in revised form
23 September 2013
Accepted 28 September 2013
Available online 12 October 2013

Keywords:
Metallophtalocyanine thin film
Metallophtalocyanine nanostructures
Physical vapor deposition
Annealing process
Phase change
Second harmonic generation

ABSTRACT

The paper presents the second order nonlinear optical properties of Cu, Co, Mg and Zn metallophtalocyanines thin films. The films were fabricated by physical vapor deposition in high vacuum onto fused silica glass substrates. In order to investigate both optical and structural properties an annealing process in an ambient atmosphere for 12 h at temperatures equal to either 150 °C or 250 °C applied after the fabrication process. Atomic force microscopy images were obtained for an observation of the structural property changes. The thickness of the thin films was in the range from 80 nm to 120 nm. The size and shape of the forming nanostructures were different for different metallophthalocyanines and depended on the phase of the material. As-deposited sample of copper phthalocyanine formed the smallest nanostructures – standing columns with 100 nm of the height and 40 nm of the diameter. Annealed sample formed the largest nanostructures – lying cuboids with dimensions: 10 × 1000 × 40 nm. The second harmonic generation measurements have been carried out in order to investigate the second order nonlinear optical properties and their dependence on the structure of the thin films after the annealing process. Moreover the fittings based on the two models have been carried out in order to understand deeper the origin of the experimental findings. It was found that the annealing process can significantly modify both the structural and the second order nonlinear optical properties of the metallophthalocyanine thin films.

1. Introduction

During the last few years, organic nonlinear optical materials have gained a great deal of research interest, because they offer several advantages such as large nonlinearities, fast response and low losses compared to inorganic materials [1–4]. These properties play a very important role in applications in optoelectronics, photovoltaic and photonic devices including flat-screen TVs, e-book readers, optical storage, optical switching, organic thin film transistors, organic photovoltaic devices, holography, biosensors, optical communications, solid-state lighting, but also in harmonic generation and photosensitizers for photodynamic therapy [5–11].

Second order optical nonlinearities in organic compounds derive from a highly polarizable charge asymmetry of a π-conjugated system restricted to groups of different electron affinities. The polarization is a nonlinear function of the applied field and the efficacy of the molecule to be polarized asymmetrically is represented by its first order hyperpolarizability. The second order nonlinear optical effects can occur only in molecules lacking an inversion center. A bulk material, thin film or nanostructures composed of nonlinear molecules must also lack a center of symmetry to exhibit second order optical properties, which can be defined by the second order optical susceptibility $\chi^{<2>}_{\mathrm{eff}}$. Moreover, these materials should exhibit low optical losses and they have to be thermally, physically and photochemically stable for industrial applications [12,13].

Phthalocyanines (Pcs) are very special organic materials because of their variety, architectural flexibility and exceptional environmental stability. Pcs offer great opportunities to adapt their properties over a wide range either by substituting different metal atoms into the ring or by altering peripheral and axial functionalities. This substitution facilitates the tailoring of physical parameters of metallophthalocyanines (MPcs) over a broad range and,

---

* Corresponding authors.
E-mail addresses: azawa@fizyka.umk.pl (A. Zawadzka), bouchta.sahraoui@univ-angers.fr (B. Sahraoui).

0143-7208/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.dyepig.2013.09.044

consequently, allows modulating the physical, electrical and optical behavior of the compounds. Phthalocyanines can adopt more than 70 different metallic and non-metallic ions into the ring cavity [14].

Metallophthalocyanines represent a large family of materials with centrosymmetric planar structure of 16 member rings with 18 delocalized π-electrons which leads to their special optical properties and extraordinary stability [15–17]. The metal-free phthalocyanine forms completely planar molecular structure with a cavity diameter equal to 393 pm. Studies on MPcs are often focusing on the position of the central metal in relation to the 16-membered ring C_8N_8. Most of MPcs complexes have a planar coordination around the central ion, which means that the metal and ligand atoms are generally in one plane. These MPcs molecules possess approximately D_{4h} symmetry. However, there are also cases where the large metal ions adopt a position outside the plane of the ring and significant doming occurs, giving these molecules C_{4v} symmetry. The diameter of the phthalocyanine cavity can also fluctuate. Table 1 illustrates these effects. From these differences in geometries of MPcs, four different states of the phthalocyanine ring are identified: metal ion size smaller than the phthalocyanine cavity size, metal ion size approximately equal to phthalocyanine cavity size, metal ion size greater than phthalocyanine cavity size and metal ion size much larger than phthalocyanine cavity size. These four states exhibit four structural effects of the phthalocyanine ring: ring contraction, equilibrium ring geometry, ring expansion and metal non-planarity.

This article is devoted not only to second order nonlinear optical properties of Physical Vapor Deposition (PVD) deposited MPcs thin films and nanostructures (where M = Co, Cu, Zn and Mg), investigated by Second Harmonic Generation (SHG) technique, but also to the structural properties of the generated nanostructures as a function of the applied temperature during the annealing process and mutual correlations between the structural and nonlinear optical properties. The aims was achieved in this work through theoretical and experimental investigation of the Second Harmonic Generation (SHG) of the systems, which sheds light into the differences in the nonlinear optical spectra of MPcs after the annealing process and Atomic Force Microscopy (AFM) in order to investigate thin film structure before and nanostructures after the annealing. To reach this goal, four different MPcs have been investigated. Three of them: copper phthalocyanine (CuPc), cobalt phthalocyanine (CoPc) and zinc phthalocyanine (ZnPc) contain 3d electron shell of the metal atoms. CuPc and CoPc form flat molecular structure with D_{4h} symmetry, while ZnPc forms non-planar (zinc metal adopt position out of the plane) molecular structure with C_{4v} symmetry. MgPc forms flat molecular structure with D_{4h} symmetry, but the central metal lacks d electrons. Investigation was focused on metallophthalocyanines (MPcs) because the substitution of different metal atoms into the ring should lead to changes in the structural and linear/nonlinear optical properties of the thin films. The long-range aim of this study is to learn how the substitution of the different metal atoms into the ring of the MPcs correlate with the nonlinear optical properties and also to enhance those properties via control of the nanostructures forming inside thin film's during annealing process.

Table 1
The variation in phthalocyanine cavity size and the non-planarity of large metal ions in simple metallophthalocyanines.

Compound	Cavity diameter [10^{-10} m]	Distance of M from N_α plane [10^{-10} m]
H_2Pc	393	0
MgPc	374	0
MnPc	387	0
FePc	385	0
CoPc	382	0
NiPc	366	0
CuPc	386	0
ZnPc	396	7.5
SnPc	393	118
PtPc	396	121
PbPc	395	125

2. Experimental methods

2.1. Deposition of thin films and nanostructures

The all investigated MPcs thin films and nanostructures were fabricated by PVD technique using typical vacuum evaporation equipment [18–22]. The thin films have been deposited on a fused silica glass substrate. The process of the deposition has been carried out under pressure of approximately $2*10^{-5}$ Torr. Powders of the source material (CoPc, ZnPc, CuPc and MgPc, 97% Sigma–Aldrich Co.) were loaded onto a quartz effusion cell with a nozzle diameter equal to10 mm. The materials were thermally evaporated from a quartz crucible heated by tungsten resistance coil. The temperature of evaporation source has been manually controlled (using K-type thermocouple and autotransformer). Temperatures of source for metallophthalocyanines materials are presented in Table 2. The glass plates were located on the substrate holder about 10 cm above the evaporation source. The film thickness during the thermal evaporation depends on the evaporation's time and the distance between source and substrate. Our deposition system assures approximately 80% accuracy of the desired value of the film's thickness. The deposition rate was in the range 0.1–0.2 nm/s and depended on the source material and temperature. The thickness of the fabricated MPcs thin films was in a range from 80 to 120 nm. The substrates were held at room temperature during the evaporation's process. Selected thin films underwent an annealing process to assure a different morphology of the films and related nonlinear optical properties.

2.2. Characterization of thin films and nanostructures

SHG measurements were carried out using the rotational Maker fringe technique [23] in the transmission scheme shown in Fig. 1. A quartz plate has been used as a reference material for the second harmonic generation measurements. A Q-switched mode-locked Nd:YAG laser operating at 1064 nm with 16 ps pulse duration, 1.6 mJ power per pulse and repetition frequency of 10 Hz was used as a fundamental beam. The laser beam has been found to exhibit Gaussian spatial and temporal profile. The beam's diameter was 0.4 mm at the film and the applied power density was about 5 GW/cm^2. A half wave plate placed before the polarizer controlled the polarization and the power density of the beam. The fundamental beam was focused on the sample using a lens with 250 mm focal length. A rotation stage with a resolution of 0.5° (model Standa 8MR180) with the mounted sample of MPc allowed the variation of the incidence angle. After passing the sample, a transmitting filter (FL532) permitted to preserve only the second harmonic (at

Table 2
Parameters of PVD process for MPcs thin films.

Sample	Temperature of deposition [°C]	Time of deposition [min]	Thickness [nm]
CuPc	350	20	100
MgPc	340	20	120
ZnPc	360	15	90
CoPc	360	15	80