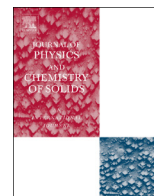




ELSEVIER

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

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

Investigation of optical properties of annealed aluminum phthalocyanine derivatives thin films

M.E. Sánchez-Vergara ^{a,*}, M. Rivera ^b^a Facultad de Ingeniería, Universidad Anáhuac México Norte. Avenida Universidad Anáhuac 46, Col. Lomas Anáhuac, 52786 Huixquilucan, Estado de México, Mexico^b Instituto de Física, Dpto. Materia Condensada, Universidad Nacional Autónoma de México, Coyoacán, 04510 México, D.F., Mexico

ARTICLE INFO

Article history:

Received 22 July 2013

Received in revised form

5 December 2013

Accepted 8 January 2014

Available online 30 January 2014

Keywords:

A. Thin films

A. Electronic materials

D. Optical properties

ABSTRACT

Semiconducting molecular materials based on aluminum phthalocyanine chloride (AlPcCl) and bidentate amines have been successfully used to prepare thin films by using a thermal evaporation technique. The morphology of the deposited films was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Studies of the optical properties were carried out on films deposited onto quartz and (1 0 0) monocrystalline silicon wafers and films annealed after deposition. The absorption spectra recorded in the UV–vis region for the as-deposited and annealed samples showed two absorption bands, namely the Q- and B-bands. In addition, an energy doublet in the absorption spectra of the monoclinic form at 1.81 and 1.99 eV was observed. A band-model theory was employed in order to determine the optical parameters. The fundamental energy gap (direct transitions) was determined to be within the 2.47–2.59 and 2.24–2.44 eV ranges, respectively, for the as-deposited and annealed thin films.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Heterostructures, whose building blocks are van der Waals interacting materials, have been strongly addressed in recent years due to their potential applications. Among the organic molecules interacting via van der Waals forces, metal phthalocyanines (MPcs) play an important role [1]. MPcs are mainly highly colored organic p-type semiconducting compounds. However, there are n-type materials such as cobalt(II) hexadeca-fluoro-phthalocyanine (F₁₆CoPc), among others [2]. MPcs exhibit high chemical and thermal stability and thus can be sublimated without decomposition to form high-quality thin films by means of the thermal evaporation technique [3]. These thin films have proven to possess great potential as materials for optoelectronic and electronic devices for organic solar cells, field effect transistors, molecular gas sensors, organic light-emitting diodes (OLED), organic memories, semiconductor layers or optical limiters [4–13]. The optical properties of MPcs thin films are known to be critically dependent upon a variety of parameters including purity, crystal structure, morphology and device temperature, among others [4]. In addition, since they are very good light absorbers in the UV–vis region, they are widely used as excellent laser dyes capable of optical amplification in the red region of the visible spectrum [4–14].

MPc (C₃₂H₁₆N₈-M) is a planar molecule with a porphyrin-like central structure bonded to four aromatic rings with a central metal atom [1]. MPcs show several crystalline polymorphs including the α-, β- and γ-structures [14]. Depending upon the deposition conditions, different molecular orientations and crystalline structures can be obtained [8]. Materials deposited at room temperature are crystallized in the α-phase and can be transformed into a different crystalline form by post-annealing or by using a higher substrate temperature during deposition [4]. Post-annealing or deposition at high substrate temperatures usually leads to the formation of the more stable β-phase [4,15]. The absorption spectra of different polymorphs of some phthalocyanine compounds show significant differences among each other. Relatively few studies have focused on halogenated MPcs [4,16–18]. It has also been shown that halogenated phthalocyanines exhibit remarkable morphological and thermal stability over a large temperature range, compared to unhalogenated phthalocyanines [4,16–18].

In the present work, the synthesis and film formation of semiconductors from the reaction of aluminum phthalocyanine chloride (AlPcCl) and bidentate amines 1,4-diaminobutane and 1,4-diaminoanthraquinone (Fig. 1) were achieved. The films were prepared by thermal evaporation and characterized by IR spectroscopy, AFM, SEM, EDS and ellipsometry. In this communication, we determined the optical parameters related to the main transitions in the UV–vis region, as well as the corresponding fundamental energy gaps for the thin films. The refractive indices and absorption coefficients, parameters of particular interest for the design and fabrication of optoelectronic devices, were also obtained for the films.

* Corresponding author. Tel.: +52 55 56 27 02 10x8242;

fax: +52 55 53 28 80 67.

E-mail address: elena.sanchez@anahuac.mx (M.E. Sánchez-Vergara).

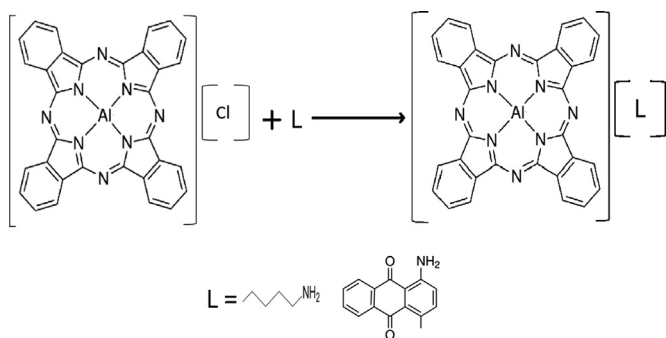


Fig. 1. Chemical structures of the synthesized molecular materials obtained from AlPcL. L=BDA, AqDA.

2. Experimental details

2.1. Synthesis: starting material and chemicals

All reagents employed were acquired from Sigma-Aldrich Chemical Co., Inc. The reagents were used without previous purification. A series of AlPcL were synthesized by a simple anion exchange reaction. A solution of AlPcCl ($C_{32}H_{16}AlClN_8$) in absolute ethanol was added to a solution of the appropriate diamine ligand 1,4-diaminobutane ($C_4H_{12}N_2$) or 1,4-diaminoanthraquinone ($C_{14}H_{10}N_2O_2$) in the same solvent (Fig. 1). The resulting mixture was maintained under reflux for about three days until a precipitate was obtained. Next, the product was filtered, washed with absolute ethanol and then vacuum-dried. The product was purified from a 1:1 ethanol-water solution. The IR spectroscopy characterization of powdered materials was carried out by means of a Nicolet iS5-FT spectrophotometer using KBr pellets for solid samples within the $4000\text{--}300\text{ cm}^{-1}$ region with an 8 cm^{-1} resolution.

Compound 1. 0.30 g (0.52 mmol) of AlPcCl in 30 mL ethanol, 0.092 g (1.04 mmol) of 1,4-diaminebutane in 30 mL ethanol. Green powder, yield 72%. m.p. 581 K (dec). Calculated analysis for $C_{36}H_{26}N_9Al$: C, 70.70%, N, 20.62%, H, 4.25%; Found: C, 69.96%, N, 19.89%, H, 4.30%;

Compound 2. 0.30 g (0.52 mmol) of AlPcCl in 30 mL of ethanol, 0.25 g (1.04 mmol) of 1,4-diamineanthraquinone in 30 mL ethanol. Blue powder, yield 79%. m.p. 583 K (dec). Calculated analysis for $C_{46}H_{24}N_9O_2Al$: C, 72.54%, N, 16.56%, H, 3.15%; Found: C, 72.32%, N, 16.05%, H, 3.46%;

2.2. Thin film deposition

Based upon the synthesis of **compounds 1** and **2**, by the phthalocyanine-ligand reaction, the thin film deposition process was carried out by thermal evaporation onto quartz and (1 0 0) monocrystalline silicon (c-Si) $200\ \Omega\text{ cm}$ wafers. The quartz substrates were ultrasonically degreased in warm methanol and dried under a nitrogen atmosphere. The silicon substrates were chemically etched with a *p-etch* solution (10 ml HF, 15 ml HNO_3 and 300 ml H_2O) for removing the native oxide from the c-Si surface. In order to achieve high purity thin films, a vacuum chamber was used with a diffusion pump, together with a special tungsten crucible with a double-grid cover. A quartz fiber was added inside the crucible to avoid the ejection of grains towards the substrate at a temperature of 323 K. The evaporation temperature in the boat was 453 K, which is lower than the typical decomposition temperature for these compounds. This value was measured by means of a chromel–alumel K-type thermocouple. All samples were obtained using the same deposition system, with the crucible and substrates arranged in similar geometries. The pressure in the vacuum chamber before the film deposition was measured at

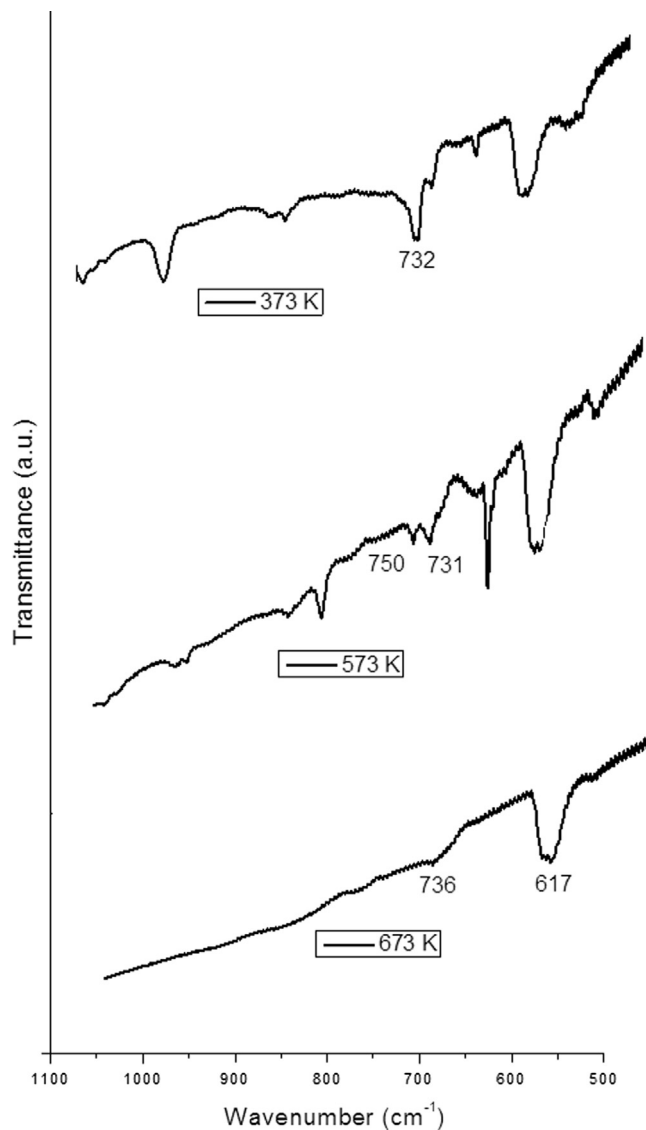


Fig. 2. IR spectroscopies obtained for **compound 1** after 2 h of annealing time at temperatures: (a) 373 K, (b) 573 K and (c) 673 K.

1×10^{-6} Torr, an evaporation rate of $70\ \text{\AA/s}$, in all cases. The thicknesses were monitored during the deposition processes using a quartz crystal monitor and were subsequently measured by ellipsometry. All the samples were annealed at a temperature of 473 K for 2 h in air with the optimal temperature and time set up based upon different annealing trials at 373, 473, 573 and 673 K for 2 h (see Figs. 2 and 5).

2.3. Thin films characterization

(i) FT-IR measurements were obtained with a Nicolet iS5-FT spectrophotometer using silicon flakes as substrates for the thin films. (ii) For SEM, a Leica Cambridge scanning electron microscope (model Stereoscan 440) was coupled to a microanalysis system and operated at a voltage of 20 kV and at a focal distance of 25 mm using thin films over quartz substrates. (iii) AFM characterization used a JEOL microscope, model JSPM-4210 in a Tapping (AFM) working mode. For the AFM characterization of the films, both quartz substrates were used. (iv) Ultraviolet–visible spectroscopy was carried out in a Unicam spectrophotometer model UV300, with a quartz substrate. (v) The film thickness and refractive index were determined by ellipsometry, which was carried out by a

Download English Version:

<https://daneshyari.com/en/article/1515797>

Download Persian Version:

<https://daneshyari.com/article/1515797>

[Daneshyari.com](https://daneshyari.com)