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Thin films of molecular materials synthesized from $C_{32}H_{20}N_{10}M$ (M = Co, Pb, Fe): Film formation, electrical and optical properties

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ABSTRACT

In this work, the synthesis of molecular materials formed from metallic phthalocyanines and 1,4-phenylenediamine is reported. The powder and thin film (~80–115 nm thickness) samples of the synthesized materials, deposited by vacuum thermal evaporation, show the same intra-molecular bonds in the IR spectroscopy studies, which suggests that the thermal evaporation process does not alter these bonds. The morphology of the deposited films was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM) and their optical and electrical properties were studied as well. The optical parameters have been investigated using spectrophotometric measurements of transmittance in the wavelength range 200–1200 nm. The absorption spectra recorded in the UV–vis region for the deposited samples showed two bands, namely the Q and Soret bands. The optical activation energy was calculated and found to be 3.41 eV for the material with cobalt, 3.34 eV for the material including lead and 3.5 eV for the material with iron. The effect of temperature on conductivity was measured for the thin films and the corresponding conduction processes are discussed in this work.

1. Introduction

In recent years, compounds formed from metallic phthalocyanines have received considerable attention due to their potential optical and electronic applications and the likelihood that these compounds may be used as organic photoconductors and in photosensors, solar cells and other devices [1,2]. The conjugated bonds and their high planarity, the high concentration of π-dislocated electrons, and the ability to form stable compounds with metallic ions [3] provide phthalocyanines with quite relevant properties, such as electrical parameters in the ranges reported for wide-band organic semiconductors [4–7]. Besides their excellent conductivity properties, phthalocyanines show very intense optical absorption values in the visible region. Thus, they are considered likely candidates for optical amplification in the 600–700-nm region [8], which makes them potentially useful for nonlinear optical applications and may lead to their use in organic-laser manufacturing. Phthalocyanines' high thermal stability permits the deposition of thin films through high-vacuum vaporization, as this method does not lead to the decomposition of the synthesized compounds [9]. The production of thin films from organic materials for device applications is relevant in this context, given the potential design simplicity, low fabrication costs, and ease of characterization in the optical and electrical domains [10,11].

A simple method has been developed to synthesize a molecular semiconductor from the chemical reaction of metallic phthalocyanines (MPc) and 1,4-phenylenediamine, followed by a thermal evaporation. In this communication, we also report the determination of important optical parameters related to the principal optical transitions in the UV–vis region, as well as the corresponding optical band gap calculations. In amorphous inorganic semiconductors, loss of periodicity and crystalline structure results in the localization of electronic wave functions and tail formation in the density of states which extends into the forbidden energy gap at the valence and conduction band edges. Electrical conduction can then be explained in terms of band theory and a hopping model establishing a mobility edge for the charge carriers [12].

2. Experimental details

All the reactants employed, i.e., metal(II) phthalocyanine, $C_{32}H_{16}N_8M$, M = Co (1), Pb (2), Fe (3); and 1,4-phenylenediamine,

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$C_6H_8N_2$ (A), were acquired from Aldrich Chemical Co., Inc. The reactants were used without previous purification. The characterization of powder materials was carried out, for IR spectroscopy, in a Bruker spectrophotometer, model Tensor 27, using KBr pills for solid samples in the 4000–300 cm^{-1} region with an 8 cm^{-1} resolution. For the preparation of thin films, Corning 7059 glass and silicon substrates and a vacuum thermal evaporator with diffusion pump were used. For the same films, FTIR measurements were obtained with a spectrophotometer Nicolet 205, using a substrate of silicon flakes, in the 4000–300 cm^{-1} range with an 8 cm^{-1} resolution. For SEM, a Leica Cambridge scanning electron microscope (model Stereoscan 440) was coupled to a microanalysis system and operated at a 20-kV voltage and a focal distance of 25 mm. AFM characterization used a Jeol microscope, model JSPM-4210, within the Tapping (AFM) work mode. UV–vis spectroscopy was carried out in a Unicam spectrophotometer, model UV300, using a Corning glass 7059 substrate. Ellipsometry was carried out in a Gaertner Scientific Corporation ellipsometer (model L117), with He–Ne laser operating at 630 nm and using silicon flakes as substrate. A four-probe press contact method was used to measure the electrical conductivity of the sample with a working-temperature range of between 360 and 473 K. The temperature dependence of the electrical conductivity of the sample in this range was measured with a Keithley 230 programmable voltage source and a Keithley 485 auto-ranging pico-ammeter, both PC-controlled. The temperature of the sample was measured with a chromel–alumel thermocouple attached to an HP 3421 data acquisition unit.

2.1. Synthesis of $C_{32}H_{20}N_{10}M$

The chemical synthesis of molecular materials started with the dissolution of the metallic phthalocyanine (compounds 1, 2 or 3) and 1,4-phenylenediamine (compound A) in 35 ml of distilled water, which was then stirred for 20 min. The solution was then set to reflux for 72 h. The resulting materials were filtered, washed with distilled water, purified and stored in a desiccator.

2.1.1. Synthesis of $C_{32}H_{20}N_{10}Co$ (material 1-A)

0.5018 g (0.000878 mol) of cobalt(II) phthalocyanine and 0.5012 g (0.0046 mol) of 1,4-phenylenediamine. Yield 87%. Calculated analysis for $C_{32}H_{20}N_{10}Co$: C 63.68%, N 23.33%, H 3.32%; Found: C 63.39%, N 24.93%, H 3.76%; mp 312 °C.

2.1.2. Synthesis of $C_{32}H_{20}N_{10}Pb$ (material 2-A)

0.5020 g (0.000697 mol) of lead(II) phthalocyanine and 0.5010 g (0.0046 mol) of 1,4-phenylenediamine. Yield 89%. Calculated analysis for $C_{32}H_{20}N_{10}Pb$: C 51.13%, N 18.64%, H 2.66%; Found: C 51.39%, N 18.82%, H 2.39%; mp 310 °C.

2.1.3. Synthesis of $C_{32}H_{20}N_{10}Fe$ (material 3-A)

0.5018 g (0.000882 mol) of iron(II) phthalocyanine and 0.5014 g (0.0046 mol) of 1,4-phenylenediamine. Yield 93%. Calculated analysis for $C_{32}H_{20}N_{10}Fe$: C 64.00%, N 23.33%, H 3.33%; Found C 64.10%, N 23.39%, H 3.28%; mp 310 °C.

2.2. Thin films

Thin films of different thicknesses, ranging from 80 to 115 nm, were prepared by the thermal evaporation technique using a vacuum chamber with a diffusion pump and a tungsten crucible at a temperature of around 563 K. The deposition was made over a Corning glass 7059 substrate which previously was ultrasonically-washed and rinsed with deionized water. Chromium electrodes and silicon flakes with no traces of silicon oxide were used. All materials were vaporized at a temperature of about 563 K and a chamber vacuum of 0.01333 Pa (1×10^{-4} Torr).

3. Results and discussion

Regarding IR spectroscopy (Table 1), all compounds show stretching vibrations at the C=C (cm^{-1}) 1624 and C=N (cm^{-1}) 1574 bonds, as is usual for this kind of compounds formed from a metallic macrocycle and the amine [13,14]. The N–H (cm^{-1}) bond around the 3386, 3395, 3405, and 3417 vibrations suggests the presence of amines that are bound to the phthalocyanine macrocycle. Moreover, NH_2 (cm^{-1}) 2914, 2920, 2930, 2942, and 2958 bonds were identified that correspond to the amine group of a tip that is not bound to the macrocycle. This had already been reported [15] for similar compounds. From the presence of amines not bound to the macrocycle, it may be inferred that the 1,4-phenylenediamine bidentate amine (compound A) joins the metallic phthalocyanines only by one side. Middle-infrared signals arising from the phthalocyanine macrocycle (cm^{-1}) 1861 band and bands at (cm^{-1}) 870, 924, typical of C–H aromatic bonds, were found in the spectrograms.

The measurements of IR on thin films were performed on films deposited over monocrystalline silicon substrates. They were used to provide evidence that the materials did not suffer chemical decomposition following the deposition by thermal vaporization. All the highly-relevant bonds, including those related to the primary N–H amines bound to the phthalocyanine macrocycle, the NH_2 amines from the tip not bound to the macrocycle, the vibrations of C=C and C=N bonds, and the aromatic C–H bonds, were located on the thin films. There are few differences between the signals identified on powder materials and those deposited on films, and this may be due to internal stress produced during the vaporization process. These results suggest that high-vacuum,

Table 1
IR (cm^{-1}) characteristic bands for powder and thin films.

$C_{32}H_{20}N_{10}Co$ (powder)	$C_{32}H_{20}N_{10}Co$ (thin film)	$C_{32}H_{20}N_{10}Pb$ (powder)	$C_{32}H_{20}N_{10}Pb$ (thin film)	$C_{32}H_{20}N_{10}Fe$ (powder)	$C_{32}H_{20}N_{10}Fe$ (thin film)
3417	3419	3415	3418	3417	3416
3405	3405	3405	3402	3408	3408
3395	3392	3400	3396	3397	3395
3386	3380	3388	3389	3388	3380
2958	2958	2960	–	2959	2953
2942	2940	2939	2939	2946	2947
2930	2938	2930	2936	2931	2931
2920	2922	2926	2926	2919	2918
2914	2914	2917	2919	2915	2915
1624	1624	1628	1630	1631	1634
1574	1574	1570	1570	1579	1578
1861	1860	1869	1860	1861	1861
925	922	881	889	924	924
870	876	721	740	870	870