Vacuum 99 (2014) 153–159

Contents lists available at SciVerse ScienceDirect

Vacuum

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

Temperature and frequency dependencies of AC and dielectric characterizations of copper tetraphenyl porphyrin thin films

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ARTICLE INFO

Article history:
Received 28 March 2013
Received in revised form
30 April 2013
Accepted 11 May 2013

Keywords:
Copper tetraphenyl porphyrin
AC conductivity
Dielectric constants
Complex dielectric modulus

ABSTRACT

The AC conductivity and dielectric properties of the copper tetraphenyl porphyrin, CuTPP films have been investigated in the frequency range 42 Hz–5 MHz and in the temperature range 303–473 K. The AC conductivity of CuTPP is controlled by the correlated barrier hopping model. The activation energy for alternating current mechanism decreases with increasing frequency which confirms the hopping conduction to the dominant mechanism as compared with the DC activation energy. The dielectric constant ε' and dielectric loss ε'' show noticeable dependence on frequency and temperature. The dielectric relaxation mechanism was explained on the basis of complex dielectric modulus.

1. Introduction

Recently, more attention has been internationally devoted to semiconducting organic compounds due to their low-cost and highly flexible alternatives to standard micro- and optoelectronic devices, such as diodes, transistors, LEDs, lasers, modulators and sensors, traditionally based on inorganic semiconductors [1].

Porphyrins are macrocycles composed of four modified pyrrole subunits interconnected at their α carbon atoms via methine bridges (=CH-) and considered to be highly conjugated systems [2]. Moreover, porphyrins in fact are thermally and chemically stable compounds and their properties can be finely tuned by simple modifications of their basic molecular frameworks [3–5]. In addition, porphyrin dyes offer the promise of widespread adoption in numerous technology areas including molecular nanowire, information storage, non-linear optical material, gas sensors, and optoelectronic devices such as photovoltaic solar cell energy converters [6].

The coordinated metal, the peripheral substituents, the conformations of the macrocyclic skeleton of porphyrins influence the coordination and the related sensing properties of these compounds [3,7]. Almost all metals present in the periodic table have been coordinated to the porphyrins [7].

The structural and optical properties of tetraphenyl porphyrin, TPP and its substitutions have been extensively studied using visible light absorption spectroscopy, Fourier transform infrared spectroscopy and scanning tunnel microscopy [8–11]. To the best of our knowledge, there are no enough efforts concerning the study of electrical (DC and AC) conduction mechanisms and dielectric properties of thermally evaporated CuTPP thin films. The aim of the present work is to study the effect of temperature and applied frequencies on electrical conductivity for CuTPP films in a frequency range 42 Hz–5 MHz and a range of temperature from 303 K to 473 K. Moreover, dielectric constants of CuTPP thin films have also been considered.

2. Experimental details

2.1. Materials and thin film preparation

5,10,15,20-Tetraphenyl-21H,23H-porphine copper (II) CuTPP was purchased from Aldrich Chem Co. and was used as received without any further purification. Thin film of CuTPP with thickness ~870 nm were prepared by thermal evaporation technique, using a high vacuum coating unit (Edward, E 306 A, England), under a pressure of about 4×10^{-5} Torr and the rate of deposition (2.5 nm s^{-1}). Evaporation of the material is carried out using a quartz crucible heated by a tungsten coil. The coating unit is supplied with a quartz crystal monitor (FTM4, Edwards), which is

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0042-207X/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.vacuum.2013.05.012

used to control the deposition rate and measurement of the thickness was obtained. The system was kept under vacuum for about 2–3 h before air admittance to the evacuated chamber to avoid the oxidation of the sample. Thin films of CuTPP were sandwiched between two ohmic gold electrodes for electrical measurements.

The structural characteristics of the powder and thin films of CuTPP were investigated by using a Philips X-ray diffractometer (model X′ pert) with utilized monochromatic CuK_α radiation ($\lambda = 1.5418$ Å) and operated at 50 kV and 40 mA. The diffraction patterns were recorded automatically with a scanning speed of 2° min^{-1}. The differential thermal analysis (DTA) measurement was carried out by the Shimadzu instrument (DTA-50) calibrated through the melting points of indium and tin in the presence of inert gas of N_2, within the temperature range from room temperature up to 873 K. The thermal measurements were repeated twice and values agreed within the experimental errors ±1 K.

2.2. AC conductivity and dielectric measurements

The AC conductivity as well as dielectric measurements of CuTPP were carried out by the aid of a programmable automatic RLC bridge, model Hioki 3532-50 LCR HiTester, in the temperature and frequency ranges of (303–473 K) and (42 Hz–5 MHz), respectively. The temperature of the tested films was recorded using Chromel–Alumel thermocouple over the entire temperature range.

3. Results and discussion

3.1. Thermal analysis of CuTPP

Thermal analysis is used to establish thermodynamic properties of the material which are essential for understanding the behavior of material under certain conditions [12].

Fig. 1 shows the differential thermal analysis (DTA) curves of CuTPP taken at a heating rate of 15 °C min^{-1} under inert gas of N_2. It is very much more satisfactory to be able to examine the CuTPP in N_2, where the organic matter peaks are suppressed, and the sample is essentially in the as received condition. This analysis is widely used to evaluate the thermal stability of materials because it requires a small amount of the material sample and entire study was over in a few hours [12,13]. The DTA curve reveals that the CuTPP has a thermal stability up approximately 477 °C (750 K). Above this degree, a sublimation of the material occurs; solid transformation into gas vapor molecules is dominated.

3.2. Molecular and crystalline structure of CuTPP film

The infrared technique has been used to check the molecular structure of CuTPP compound. Fig. 2 shows the infrared transmission spectrum of CuTPP in both powder and thin film conditions. The vibrational assignments can notice that many bands have shoulders or are quite broad, probably due to the overlapping of two or more unresolved components. The FT-IR spectra of CuTPP reveal far-reaching similarities in most of the band patterns, but some differences appear in the position, shape and relative intensity of some bands. We also observed that the characteristics skeletal vibrational modes of the TPP parent are present in all FT-IR spectra of CuTPP. In all FT-IR spectra, the peaks at 999–1005 cm^{-1} were assigned to the pyrrole ring stretching mode. The stretching vibrations of the quarter- and half-ring of the pyrrole occur at 1346–1399 and 1290–1301 cm^{-1}, respectively. The 828–888 and 551–566 cm^{-1} bands are identified as the in-plane and out-of-plane deformations of the pyrrole ring. The N–H stretching vibration of pyrrole appears as band at 3431 ± 2 cm^{-1} and should be indicative of intermolecular hydrogen bonding; the N–H band has a weak intensity for powder CuTPP while it appears high in the CuTPP thin film. In the region between 2000 and 2800 cm^{-1}, the bands are associated with C–H stretching vibration [14–16].

The crystalline structure information of CuTPP was studied using X-ray diffraction (XRD) for powder and thin film is shown in Fig. 3. XRD pattern of the powder form showed various diffraction peaks. Miller indices of all peaks and the lattice constants of CuTPP were calculated by using the CRYSFIRE & CHECKCELL computer programs [17,18]. The analysis indicates that CuTPP has the triclinic form with space group (*P-1*) and lattice constants of $a = 12.905$ Å, $b = 20.994$ Å and $c = 9.82$ Å. The unit cell volume ($=2.66 \times 10^{-21}$ cm^3). Fig.3 also illustrates the patterns of CuTPP film on glass substrate. It is clear that they also have a triclinic lattice. These patterns also indicate that the CuTPP film is partially crystallized with preferred orientation of (0 2 0) and (1 2 1). Moreover, the figure indicates that the crystallites embedded in the amorphous background.

3.3. Temperature and frequency dependencies of AC conductivity

The variation of the natural logarithm of the total conductivity, $\sigma_t(\omega)$, as a function of frequency at various temperatures for CuTPP

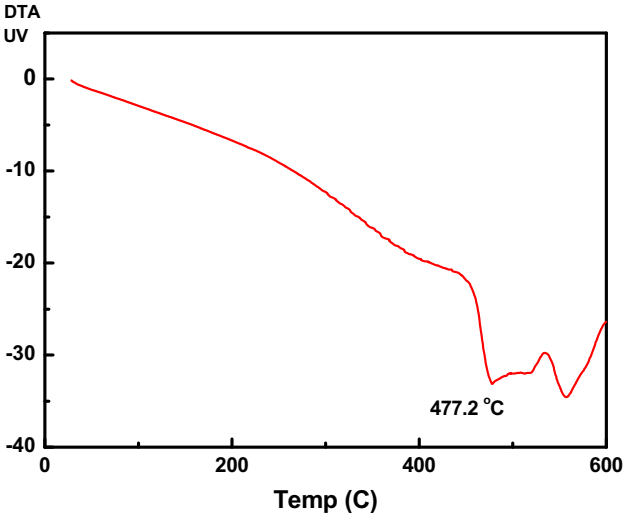

Fig. 1. Deferential thermal analysis, DTA, of CuTPP.

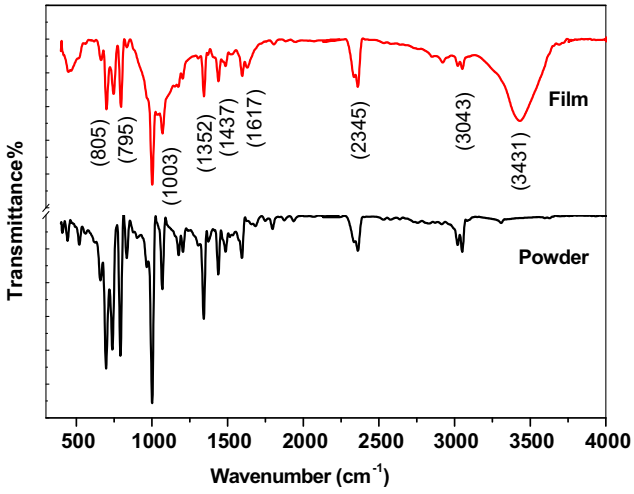

Fig. 2. FTIR spectra of CuTPP: (a) powder, (b) thin film.