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Conduction processes in tin- and silicon-phthalocyanine thin films

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Abstract

Electronic conduction studies have been carried out on evaporated tin- and silicon-phthalocyanine thin films. The samples showed carrier excitation via a field-lowering mechanism with a $\log J \propto V^{1/2}$ plot and the current density-voltage (J–V) characteristics were studied. Both polarities showed two characteristic regions in the J–V plots at low and high voltages respectively leading to the conclusion that electrical conduction proceeds via Schottky and Poole–Frenkel emission.

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1. Introduction

Organic and polymeric electronic devices have enjoyed increasing interest because of their potential low-cost applications, easy processing, great opportunity to modify their chemical structures and good compatibility with a variety of substrates. Out of them, phthalocyanine (Pcs) plays an important role as a low-gap semiconductor material. Because of the flexibility in tailoring the electrical and optical properties, phthalocyanines can be used in many devices like: fuel cells, gas sensors [1], organic metals, electronic media, photoelectrical detectors, xerographic media, field-effect transistors [2], light-emitting diodes [3–5], optical recording, optical memories, information displays [6], hole-burning memories, light-limiters, lasers, non-linear optical elements, etc. [7]. Phthalocyanines are an important class of organic materials with a very stable electronic configuration which makes them an important class of functional materials [8]. Their high stability against aggressive chemical and physical agents and other characteristic properties that they manifest have gained them a number of important applications over time. Reports on their extrinsic and intrinsic semiconductor behavior, electroluminescence [9,10], photoconductivity [11], electrochromism [12] and non-linear optical effects have appeared in the literature for many years since their discovery [13]. More recently their use in technologies such as electrophotography, laser printing and optical data storage [14–16] has already been realized and their potential in other areas such as gas sensing, charge carrying devices, electrochemical cell development and photo voltaic structures has been recognized [17].

In the solid state, the electrical behavior of Pcs can be considered as that of insulators or slightly doped semiconductors. The observation that their semiconducting properties are modulated by the absorption and desorption of gases [18] has prompted a number of

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studies towards their incorporation in gas detectors. Although the use of Pcs in this application is now well established, the basic electrical conduction processes in these materials depend on several factors that include the phthalocyanine's chemical nature, the polymorphic phase of the microcrystallites comprising the film, the film thickness, the presence of impurities or molecular doping and the electrode materials [19].

Some dc and ac studies on the conduction processes and the electrical parameters of evaporated Pc thin films have demonstrated an electrical conduction by a charge carrier hoping mechanism at low temperatures while a direct dependence on the applied voltage was predominant at higher temperatures [20,21]. In addition, it was also observed that Ohmic type conduction occurred at voltages lower than 2 V and that for voltages higher than this threshold value, the Space Charge Limited Conduction (SCLC) takes place. Other types of conduction mechanisms have been postulated for organic materials and must be considered in the elucidation of the electrical properties of new phthalocyanine materials. These mechanisms include field-lowering effects such as the Schottky and Poole–Frenkel effects, tunneling and diode-type conductivity [4,5]. In the case of field-lowering behavior, Schottky emission was identified at lower voltages, having a barrier height of 1 eV.

The study of thin-film heterostructures of the metalorganic semiconductor-metal type gives useful information concerning the electrical conduction mechanism, effective mass of the charge carriers, characteristics of metal-organic semiconductor interfaces, etc. [22]. In these systems, some interesting non-ohmic effects have been observed for high electric fields [22]. Poole–Frenkel emission was identified at higher voltages [5]. In the present work a series of I–V measurements were carried out in order to investigate the conduction mechanisms in Sn- and Si-phthalocyanine thin films.

2. Experimental

The metallo-phthalocyanines (MPc) used in this study were prepared by a highyield microwave synthetic method [24,25]. High-purity Pc material is obtained when the reaction is carried out under strictly dry conditions using an argon atmosphere. The crystalline nature of the products obtained and their chemical analysis that include IR, FAB/Mass Spectrometry and combustion analysis give evidence for the high purity of the starting materials (higher than 97%). Silicon and tin MPc films were deposited on to p-type silicon substrates having a (100) orientation, and a resistivity of 40 Ω·cm. The substrates were cleaned by conventional methods (RCA I and II) and the metallo-phthalocyanine thin films were deposited by sublimation with an Edwards Auto 306 high vacuum equipment at a pressure of 2.66×10^{-3} Pa. The thicknesses of the films were measured using a Tencor Instruments Alpha Step 200 equipment and were found to be around 350 nm. Circular aluminum electrodes were evaporated and deposited on the Pc films and onto the back of the silicon substrate up to a thickness of typically 1 μm and an area of 1.96×10^{-5} m^2. The electrical measurements were carried out at room temperature in an air ambient. Currentvoltage measurements were made using a programmable electrometer (Keithley 617) with an integral power supply. Measurements were performed in the dark, in order to eliminate photoelectric effects. Forward bias is defined as the situation when the top electrode is biased positively.

3. Results and discussion

3.1. Current density-voltage characteristics

Fig. 1 shows the dependence of current density J on applied voltage V for forward polarities. The results for reverse polarities are similar. The forward-bias current density increases very slowly with voltage up to about 2.5 V for Sn-phthalocyanine films and about 3.6 V for Si-phthalocyanine films. Above these values the rate of increase is faster. Therefore the lower voltage region can no longer be treated as Ohmic, as the slope is in the range of 0.4 for silicon phthalocyanines and 1.2 for tin Pcs. Above this voltage the slope approximates to the mean value of 2.5.

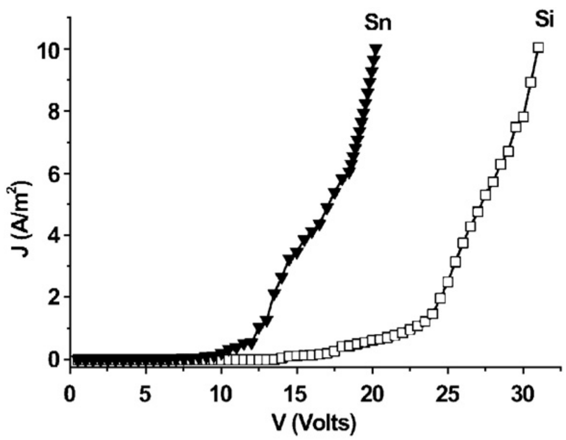

Fig. 1. Results of the dependence of current density J on applied voltage V for forward polarities.