JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 1, January 2008, p. 185 - 189

Sensing of chemical vapors by Copper Phthalocyanine (CuPc) Thin Films

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Thin films of copper phthalocyanine have been deposited onto glass substrates by thermal evaporation technique at room temperature. The electrical measurements (dc conductivity and photoconductivity) have been taken at different temperatures in the range 300-400 K. These films have been studied as chemical sensors such as methanol and ammonia. Electrical measurements indicate that these thin films have moderate sensitivity towards methanol and ammonia vapors. Infrared absorption spectra indicate that central metal ion interacts with the vapors. Coordination of vapors at fifth coordination site is responsible for the sensing properties of CuPc.

(Received May 22, 2007; accepted January 10, 2008)

Keywords: Sensor, Copper Phthalocyanine thin films, Chemical vapors sensing, Photoconductivity

1. Introduction

Recently, there has been considerable interest in exploiting organic substance such as porphyrin [1], pthalocyanine [2] and doped conductive polymers. The phthalocynine are a class of chemically and thermally stable organic semiconductors and, thus, suitable for the preparation of thin films. Metal phthalocyanine (MPcs) are very interesting for several applications, including chemical sensing [3], photo conducting agents [4], photovoltaic cell elements [5], nonlinear optics [6] etc. In the gas sensing field, MPcs are mainly used as electrical gas sensors, because of the conductivity changes induced by the absorption of oxidizing or reducing gases such as NO_x and halogens. Detection of NO_2 gas down to 25 ppb concentration by means of a lead phthalocyanine film has been attained [7]. The classical deposition methods of thin organic films such as spin coating, dip coating and sol-gel method cannot be easily applied to the production of MPcs coatings owing to the low solubility of these compounds in organic solvents, inaccurate thickness homogeneity, control and solvent retention. The solubility of MPcs can be enhanced by adding substituent groups which promote the film adhesion to the chosen substrate, but the complexity of the chemical synthesis as well as the related cost will increase. These drawbacks are avoided by using high vacuum evaporation, which has become the most widely used technique for the deposition of MPcs films.

For CuPc films, the most common polymorphs are the metastable α and the stable β. CuPc films evaporated at room temperature, at a pressure of less than 10^{-3} Pa, usually consists of α phase crystallites. At higher deposition pressures or at substrate temperatures above 210 ^{0}C, the β phase is obtained. The α phase crystallites undergo a complete transformation into β phase after annealing at temperatures higher than 250 ^{0}C [8].

2. Experimental

The CuPc thin films have been deposited by thermal evaporation technique on glass and KBr pallet for electrical and infrared (IR) absorption measurements respectively. Pre-deposited thick indium electrodes on well-degassed corning 7059 glass substrates have been used for the electrical contacts. A planar geometry of the film (length ≈ 1.78 cm; electrode gap ≈ 8 x 10^{-2} cm) is used for the electrical measurements. Thickness of the film is ≈ 7500 Å. The film has been kept in the deposition chamber in dark for 24 hours before mounting in the metallic sample holder to attain thermodynamic equilibrium. The photoconductivity of the amorphous film has been studied by mounting it in a specially designed metallic sample holder where heat filtered white light (200 W Tungsten lamp) can be shone through a transparent quartz window. A vacuum of about 10^{-3} mbar is maintained throughout these measurements. Light intensity is measured by a digital Luxmeter (Testron, model TES-1332). The photocurrent is obtained after subtracting dark current from the current measured in

presence of light. For transient photoconductivity measurements, light is shone on the thin film and the rise of photocurrent is noted manually from a digital Pico ammeter (DPM-111 Model). The accuracy in I_{ph} measurements is typically 1pA. I-V curves are symmetric and linear up to 30 V in the dark.

3. Results and discussion

Fig. 1 shows the temperature dependence of dark conductivity (σ_d) for the thin films of CuPc in the temperature range 300 – 400 K. The temperature dependence of σ_d can be expressed by the usual relation

$$\sigma_d = \sigma_0 \exp (- \Delta E_d / k T) \quad (1)$$

where ΔE_d is the activation energy for dc conduction and k is the Boltzmann's constant.

Form Fig. 1, it is clear that there are two different linear regions having different dark activation energies i.e. ΔE_{d1} = 1.58 eV and ΔE_{d2} = 0.62 eV at T <351 K and T >351 K respectively.

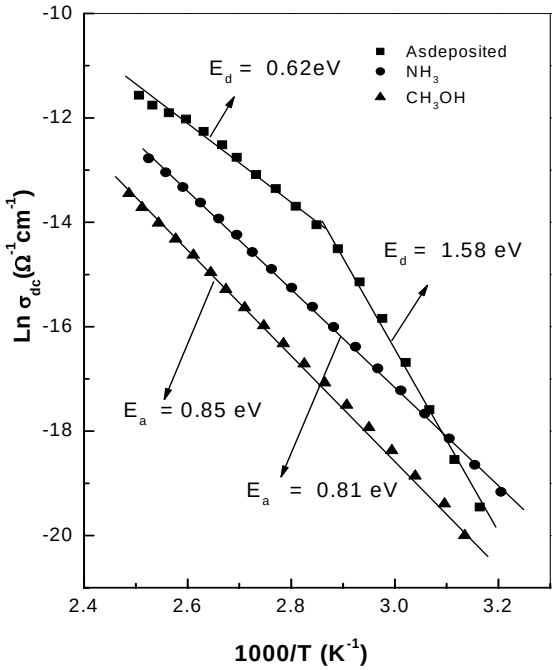

Fig.1. DC conductivity vs temperature graph of CuPc unexposed and exposed with vapors of ammonia and methanol.

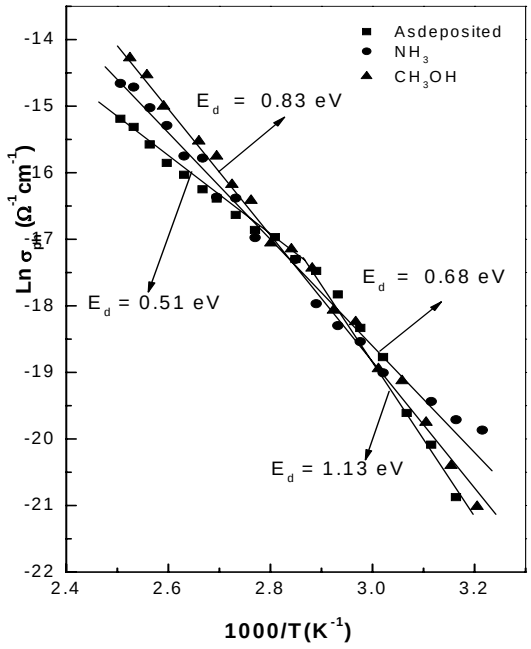

Fig. 2. Temperature dependence of photo-conductivity at different temperatures.

The dark activation energy ΔE_{d1} is associated with an intrinsic generation process and ΔE_{d2} is associated with impurity conduction. The conduction mechanism is explained in terms of hopping through bands of localized states at lower temperatures and by free conduction at higher temperatures. Hoshi et al. [9] have reported that if higher substrate temperatures are used, the Pc admolecule mobility is high and islands of bulk crystals are formed. The change in the slope and hence activation energy is interpreted as a change from extrinsic to intrinsic conduction [10]. Fig. 1 also contains the plot of ln σ_d vs 1000/T for the exposed films in methanol and ammonia vapors for 20 minutes. It is clear from the figure that the plots are hence the activation energy is interpreted as a change from extrinsic to intrinsic straight lines having single activation energies for both exposed (i.e. ammonia and methanol) films. In case of ammonia, $\Delta E_{d(ammonia)}$ = 0.81 eV and in case of methanol, $\Delta E_{d(methanol)}$ = 0.85 eV have been observed. The value of σ_d decreases from 5.79 x 10^{-8} Ω^{-1} cm^{-1} to 3.03 x 10^{-8} Ω^{-1} cm^{-1} after the ammonia exposure and 5.79 x 10^{-8} Ω^{-1} cm^{-1} to 7.84 x 10^{-9} Ω^{-1} cm^{-1} after the methanol exposure at 331 K. The decrease in conductivity in the presence of ammonia may be due to catalytic reaction of the donor ammonia, which removes the oxygen from the film. The pseudomorphic

layers formed at room temperature are in a metastable state and can be destroyed by the annealing process. When such layers are destroyed, the phthalocyanine units are free to migrate across the surface and form large crystallite islands. The relatively strong interaction between the molecule and substrate causes distortion in the electronic surface of the phthalocyanine molecule through a charge transfer interaction. Alternately it leads to the occurrence of forbidden transitions due to symmetry breaking in the pseudomorphic layers.

Fig. 2 shows the temperature dependence of photo-conductivity (σ_{ph}) for both exposed (for 20 min) and unexposed films of CuPc thin films. It is clear from the figure that a similar behaviour has been observed in unexposed thin films i.e. two different linear regions are obtained having different photo activation energies i.e. $\Delta E_{ph1} = 1.13$ eV and $\Delta E_{ph2} = 0.51$ eV at $T < 346$ K and $T > 346$ K respectively. It is also clear from the figure that the plots of ln σ_{ph} vs 1000/T are straight lines having single activation energies for both exposed films (ammonia and methanol). In case of ammonia, $\Delta E_{ph(ammonia)} = 0.68$ eV and in case of methanol, $\Delta E_{d(methanol)} = 0.83$ have been observed. The value of σ_{ph} decreases from $1.14 \times 10^{-8}\ \Omega^{-1}$ cm^{-1} to $9.01 \times 10^{-9}\ \Omega^{-1}$ cm^{-1} after the ammonia exposure and $1.14 \times 10^{-8}\ \Omega^{-1}$ cm^{-1} to $3.06 \times 10^{-9}\ \Omega^{-1}$ cm^{-1} after the methanol exposure. The decrease in conductivity in the presence of ammonia may be due to catalytic reaction of donar ammonia which removes the oxygen from the film.

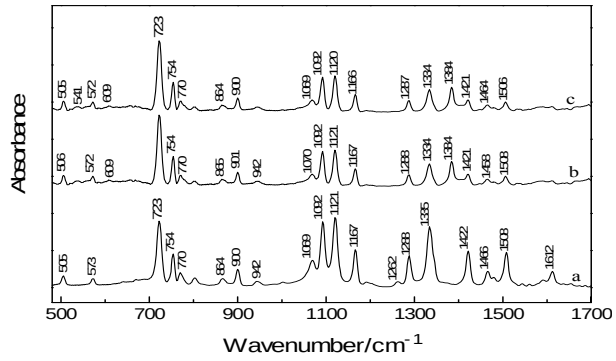

Fig. 3. Infrared spectra of CuPc thin film (a) as-deposited; (b) exposed to ammonia; and (c) exposed to methanol in 480-1700 cm^{-1} region

Infrared (IR) spectra of CuPc thin film under different environmental conditions are shown in Fig. 3. CuPc in molecular form has D_{4h} symmetry as can also be seen from its molecular structure shown in Fig. 4. Density functional theory calculation on the structure of this molecule also resulted in D_{4h} structure [11,12]. The infrared spectra of this sample, therefore, have intense bands due to two symmetry species; out-of-plane A_{2u} and in-plane E_u, which are allowed under this point group. Few weak bands, which are forbidden under D_{4h} symmetry, can also be seen in the spectra of thin film. The IR bands in 700-800 cm^{-1} in the CuPc are often used to identify different polymorphs α, β, ε etc, since these bands are sensitive to crystal packing arrangements present in the crystalline thin films [13-16]. Crystal parameter marker bands are observed at 723, 754 and 770 cm^{-1}. Observation of these bands confirms that α- crystalline form is predominantly present in the thin film, with a very small percentage of the β-form, which can be inferred from the shoulder at 780 cm^{-1} band. The presence of α- crystallite predominantly in the thin film is also

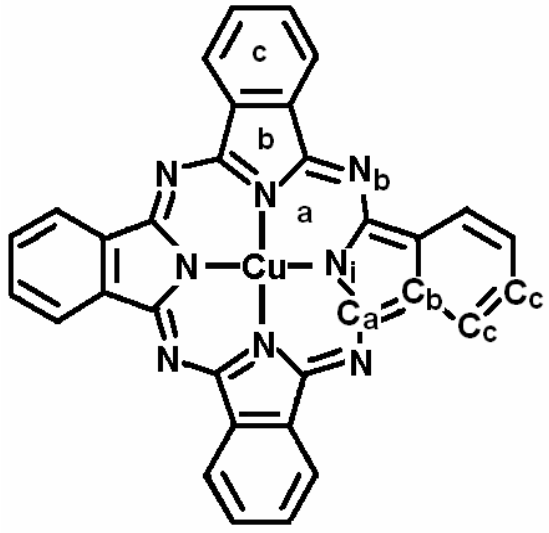

Fig 4. Structure and atom labelling of CuPc

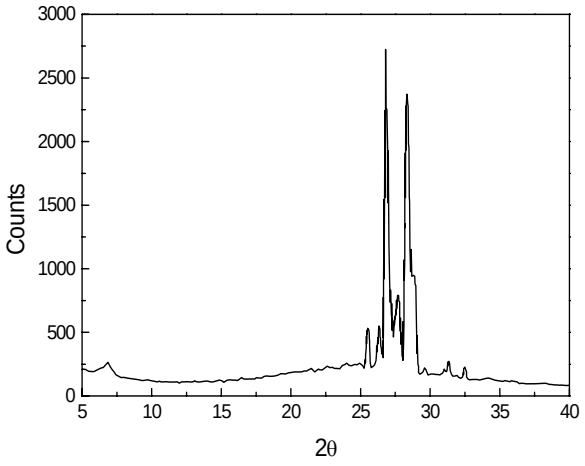

Fig. 5. XRD spectra of as-deposited CuPc thin film

supported by the appearance of unresolved bands at 864 and 870 cm^{-1} and a broad band at 942 cm^{-1}. Further evidence of the simultaneous presence of both α and β crystalline CuPc in thin film is provided by the X-ray diffraction (XRD) study. Fig. 5 shows the XRD spectrum of the thin film obtained with the Cu K_α line. The α-phase is characterized by a broad peak at d=12.89 Å and other peaks at d=3.49, 3.32 and 3.22 Å, whereas peaks due to β-phase can be seen at d=3.39, 3.15, 3.09, 3.02, 2.86 and 2.76 Å. The 723 cm^{-1} and 770 cm^{-1} bands can be assigned to out-of-plane wagging motion of C-H bonds. The former band also has contribution from C-N out-of-plane vibrations. Band at 754 cm^{-1} may be assigned to heaving motion of N_i-N_i atoms and C_a-N_i-C_a in-plane bending. In the presence of chemical vapors relative intensity of this band is decreased, which indicates towards the change in the symmetry of CuPc. However, position of these bands remains unchanged when thin film is exposed to the vapors of different chemicals. This observation suggests that the crystal packing arrangement of CuPc remains almost identical in the presence of chemical vapors. It is evident from the spectra that the intensity of a band around 1384 cm^{-1}, assigned to Cu-N_i stretching and C_a-N_b-C_a in-plane bending mode of A_{1g} symmetry under D_{4h}, is increased manifold in the presence of chemical vapors such as ammonia and methanol. The changed intensity of this band indicates towards possible change in the symmetry of CuPc due to interaction of this material with different chemical vapors. It is well known that ammonia and methanol are coordinating compounds. Therefore, vapors of these solvents may attach at the fifth coordination site of the Cu metal ion as observed in case of pyridine [17]. This interaction may move Cu ion slightly out of the mean Pc plan, thus reducing the effective symmetry of CuPc from D_{4h} to C_{4v}. Under new point group A_{1g} species will correlate to A_1 species, which become IR allowed. Therefore, increased intensity of this band can be explained on the basis of interaction of CuPc with other chemicals. Moreover, band of E symmetry at 1335 cm^{-1}, which also has contribution from asymmetric deformation from the C_a-N_i-C_a bonds. It is observed with reduced intensity in the spectra of exposed thin films. This observation further lends support to the lowering of molecular symmetry of CuPc molecules of the exposed film. It is well known that CuPc is a *p*-type organic semiconductor [19]. Methanol and ammonia molecules have lone pair of electrons, which can be transferred to other electron accepting molecules such as CuPc. When Methanol or ammonia is attached to the fifth coordination site of Cu ion, some electron density from the coordinating molecule is transferred to the empty d-orbital of the metal. This reduces the number of holes in the sample with concomitant decrease in the conductivity of the material as observed by us. This further justifies our point that these chemical vapors are attached at out-of-plane coordination site of Cu ion.

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