RESEARCH ARTICLE

Copper Tetra-Tert-Butyl Phthalocyanine Thin Films for Ammonia Gas Detection

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Abstract

Thin films of copper tetra-tert- butyl Phthalocyanine (CuPc) have been prepared from their solution in chloroform using spin coating technique. Films then heated to (100, 200 and 300) ºC to study the effect of annealing temperature on the characteristics of the prepared films. UV-visible spectrophotometer was used to investigate the absorption properties of the materials as well as the optical energy gaps. The morphology characteristics have been carried out utilizing atomic force microscopy (AFM). To demonstrate the sensing properties of CuPc films, I-V measurements were carried out using Keithly 2400 instrument to calculate the resistance before and after exposure to ammonia odorant. The prepared samples show a decrease in the resistance values after exposure to the contaminated air. Time dependency was also carried out to investigate the response and recovery time of the prepared device.

Keywords: *Copper phthalocyanine, Thin films, Gas sensor, Ammonia detection.*

Introduction

Organic materials like copper phthalocyanine (CuPc) have recently attracted a great interest as semi conducting materials [1, 2], and have been successfully integrated into optical limiters [3], solar cells [4], and chemical sensors [5]. A great deal of attention has been focused on the synthesis of phthalocyanines (Pcs) and their metallo-derivatives due to its unique color, low manufacturing cost, high stability and non-toxicity [6].

In comparison with inorganic materials, the ionization potentials, solubility, optical and molecular properties of these molecules can be easily tuned by changing the metal ion and/or by functionalizing them with different chemical groups [7].

Phthalocyanines (Pcs) in general and their metallo-derivatives (MPcs), in particular, can function as an active component in various optoelectronics applications. Another advantage of (MPcs) is their process-ability in thin films structure, which means the possibility to deposit these compounds utilizing different ways, such as spin-coating, drop-casting, thermal evaporation, and Langmuir-Blodgett techniques [8, 9].

The electrical conductivity of phthalocyanine thin films can be changed by the presence of oxidizing or reducing gases. These characteristics led to the development and application of these organic materials in the gas sensing field [10, 11]. One of the most studied metal substituted phthalocyanines is copper phthalocyanine (CuPc).Copper phthalocyanine (CuPc) is typical p-type semiconductor material which is of great value in many applications including gas sensing [12], organic light-emitting diodes [13], field-effect transistors [14], organic solar cell and other optical devices [15].

Due to their unique chemical stability and thermal stability, it can be deposited as high purity thin films using spin coating method without decomposition [16-18]. Adsorption of organic vapours or gaseous species on the surface of MPcs thin films induces changes in the electrical conductivity of Pc films [19, 20]. It has been observed that the p-type MPcs thin films of cobalt, nickel, iron, zinc and copper shows different variations in their electrical conductivities with adsorption of different electron-accepting and electron-donating gases.

Therefore on account of significant variations in electrical conductivities of these organic films after exposure to organic vapours or gaseous species; they are utilized as chemical sensors [21, 22]. Volatile organic compounds cause throat, nose, and eye irritation. Among these hazardous gases, amines complexes are commonly used in agricultural, pharmaceutical, dye manufacturing, and food processing industries. Ammonia (NH_3) is a toxic gas present in large quantities of air, soil, and water [23, 24]. The current work focuses on the characterization of copper phthalocyanine thin films and their ability to detect ammonia gas as a resistance-based device.

Experimental

We can indicate of sample preparation, and the system use to gas sensor in following:

Sample Preparation

Copper (II) 2, 9, 16, 23-tetra-tert-butyl-29H, 31H-phthalocyanine (CuPc), has been used without further purification, was purchased from sigma-Aldrich. CuPc was dissolved in chloroform in the concentration of 5 mg mL^{-1}. The mixture was sonicated for 15 min to obtain a homogenous solution. The deposition of thin films of CuPc was achieved on glass substrates using spin coating technique at 2000 rpm. Before thin films deposition, glass slides substrates were cleaned ultrasonically by dipping them in acetone for the removal of organic impurities. After films deposition, samples were annealed in a programmable vacuum oven at different temperatures (100, 200, and 300) °C for 10 minutes to study the influence of heat treatment temperatures on the properties of CuPc films.

Gas Sensor System

For the study of sensing characteristics of CuPc thin films, the electrical measurements and the time dependency results were carried out using LabVIEW software interfaced with Keithly 2400 sourcemeter. Interdigitated electrodes (IDEs) from Drop-sense Company were used for the electrical and sensor measurements. Before sensing studies, a thin film of CuPc was spin-coated at 2000 rpm on (IDEs) and heated at different temperatures (100, 200, and 300) °C. The dimensions of the IDEs are: W is the overlapping distance between the fingers (7 mm), n is the number of fingers (250) and L is the space between electrodes (5 μm).

Results and Discussion

From the research we can put the results and discussion below.

UV-visible Spectrophotometer

UV-visible absorption spectra were recorded on Shimadzu 1800 UV-visible spectrophotometer. It was shown earlier that the spin-coating method provides a convenient procedure for preparing ordered films of the phthalocyanines which can be heated to form thin liquid-crystalline films [9, 18]. Figure 1.represents the UV-visible absorption spectrum of CuPc-solutions in chloroform. The spectrum is characterized with two very strong absorption areas, first of them which is in the visible region, in the wavelength range of (650-720) nm (Q-band) arising from the electron transitions from highest occupied molecular orbital (HOMO) au$_1$ to the lowest unoccupied molecular orbital (LUMO) eg and the other (B-band) is in the near UV- region (300-450) nm (B-band) which is attributed to the electron transitions from the (HOMO) au$_2$ to the (LUMO) eg [8].Furthermore, absorption within the Q-band is split into two absorption peaks, one with much higher intensity than the other.

This can be ascribed to dominant monomer absorption with the lower intensity shoulder being ascribed to molecular aggregation in chloroform solution [25, 26]. In the Q-band, the high-energy peak is related to the π-π* orbitals interaction of the phthalocyanine macrocycle [27], while the low-energy peak may be explained as a second π-π* interaction (charge-transfer excited state) [8]. Nevertheless, the Q-band is strongly localized on the phthalocyanine ring and is very sensitive to the environment of the molecule and to changes in the orientation of the nearest-neighbor Pcs in the crystal [28].

Figure 1: UV-visible absorption spectrum of CuPc solutions in chloroform

UV-vis spectroscopy was used further to investigate the absorption spectra of the thin films of phthalocyanine deposited from their solution in chloroform using spin-coating technique. Further investigation has been carried out on the annealed films at (100,200, and 300) °C in order to demonstrate the effect of heating on absorption peaks as will the transition states. Figure 2 shows the spectra of the as-deposition films of phthalocyanine and the heated films at (100,200, and 300) °C. The electronic absorption spectra of phthalocyanines in the solid state are strongly susceptible to exciton coupling effects and these are critically dependent upon molecular packing. It has been suggested that the UV–vis spectrum of CuPc originates from the molecular orbitals within the aromatic 18-π-electron system and from overlapping orbitals on the central metal [29, 30]. The Q-band structure is more complex than that observed in the solution phase where non-aggregated phthalocyanines give rise to a single main band assigned to the doubly degenerate transition au_1-eg. In the optical spectra of CuPc films the main absorption bands are broadened through exciton coupling effects which also lead to shifts in the band positions. These are dependent upon molecular packing [31, 32]. Absorption spectra of heated films give rise to both a red- and a blue shifted band consistent with exciton splitting arising from the presence of translation ally non-equivalent molecules in the 'unit cell', as in a herringbone arrangement of molecules within adjacent columns [29].
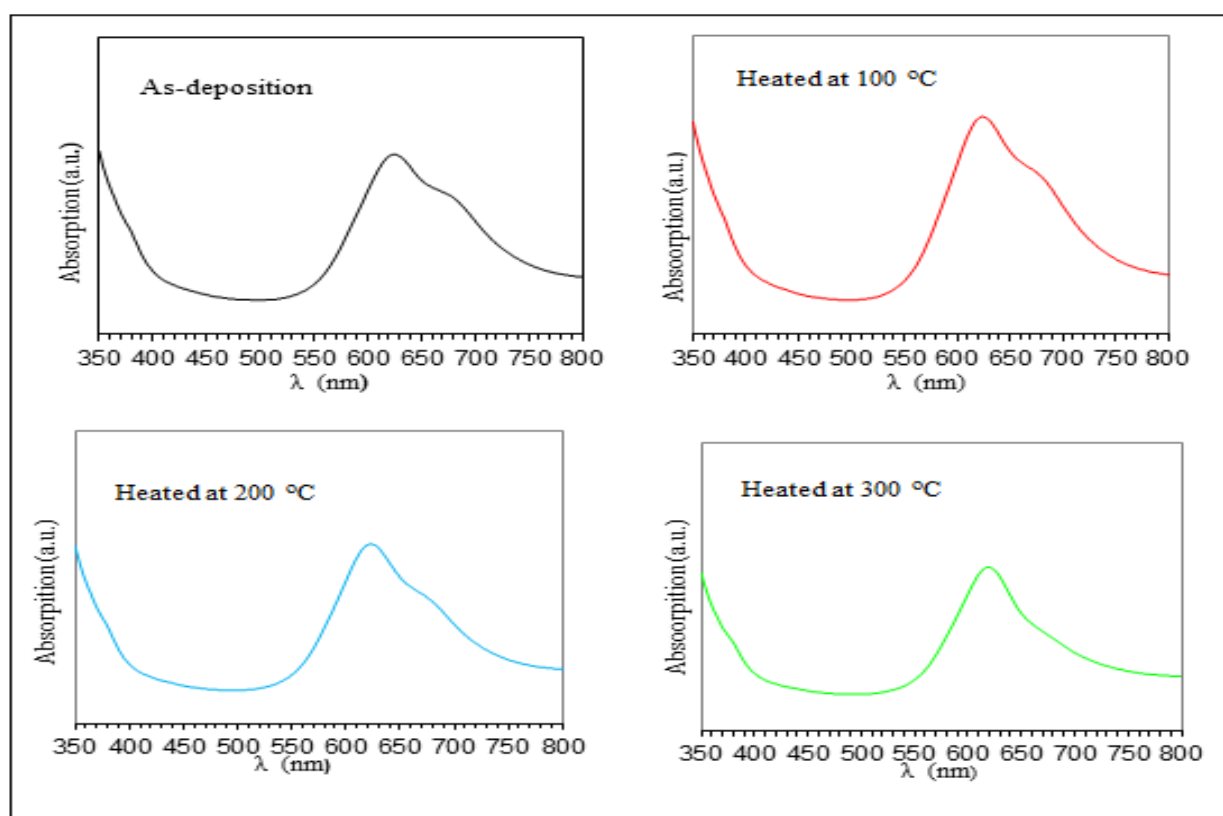

Figure 2: Optical absorption spectra for CuPc thin films deposited at room temperature and annealed at different temperatures

The Optical Band Gap

The optical band gap of the CuPc thin films has been estimated by performing a fit to the exponential part of the spectra (Figure 3) using the equation for allowed direct transitions [30]:

$$\alpha = A\left(h\upsilon - E_g\right)^r \tag{1}$$

Where A is a constant and Eg is the optical band gap energy of the semiconductor. The r determines the type of transitions which is equal to 1/2, 2 or 3/2 for direct, indirect or forbidden transitions, respectively. The dependence of $(\alpha)^{1/r}$ on the photon energy (hυ) for onset gaps are plotted from the transmission spectra of CuPc thin films. For different values of (r), the best fit was obtained for r = 1/2. The direct energies for CuPc thin films at different annealing temperatures are listed in Table 1.

Table 1: The optical band gap of CuPc films at annealed at different temperature

Sample no.	Annealing temperature (ᵒC)	Time of annealing (min)	λ_{max} (nm)	E_g (eV)
1	As-deposited	-------	615	1.804
2	100	10	617	1.773
3	200	10	614	1.795
4	300	10	611	1.850

From Table 1, results show that the optical band gaps were dependent on annealing temperature. It has been observed that band gap decreases at (100 and 200) ᵒC annealing temperatures. This can be explained as the phthalocyanine molecules oriented to a more ordered films after heating and this behavior results in straight electron channels leading to a decrease in the energy gap. However, the energy gap return to its highest value after annealing at 300 ᵒC due to exceeding the transition temperature and softening the phthalocyanine films [28].
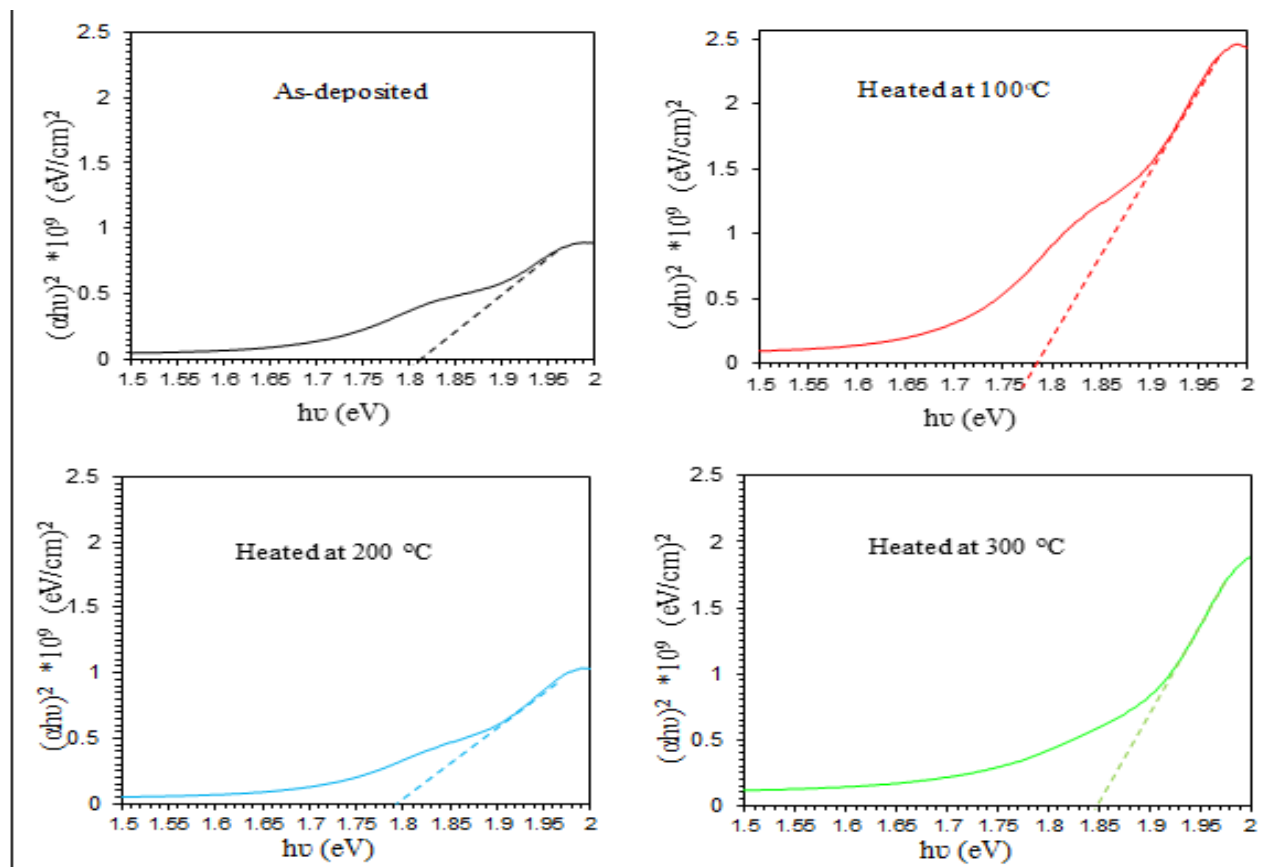
Figure 3: $(\alpha h\upsilon)^2$ against energy gap $h\upsilon$ in eV for CuPc thin films before and after annealing

Atomic Force Microscopy

Figure 4 shows AFM images of the CuPc films prior and after annealing. These images show the variation of the grain sizes and transition from one to other morphology at heat-treated films. The surface roughness was found to be Ra = (10.1, 11.7, 10.4, and 9.2) nm for the as deposited, and heated to (100, 200, and 300) ᵒC respectively. The image in the as-deposited film shows an agglomeration of grains to form small clusters. The cluster size increased on annealing the film at 100 ᵒC producing larger rod-like structures rather than clusters compared with as-deposited film .The reason for that, at higher temperature as a rule nucleation rate decreases, but lateral growth increases due to higher mobility of the adsorbed molecules and preferred unidirectional attachment of the molecules. This preferential direction comes from the interaction of weak Van der Walls forces and π-π interactions along adjacent molecules, which give rise to larger sticking coefficient along this direction [33]. These conditions lead to anisotropic rod-like grains with large lateral dimension. At 200 ᵒC the interconnectivity and parallel growth of the grains are observed to be decreasing though the elongation exits till 300 ᵒC. This suggests that on increasing the substrate temperature the film start making a transition from polycrystalline to single crystalline growth [33, 34].
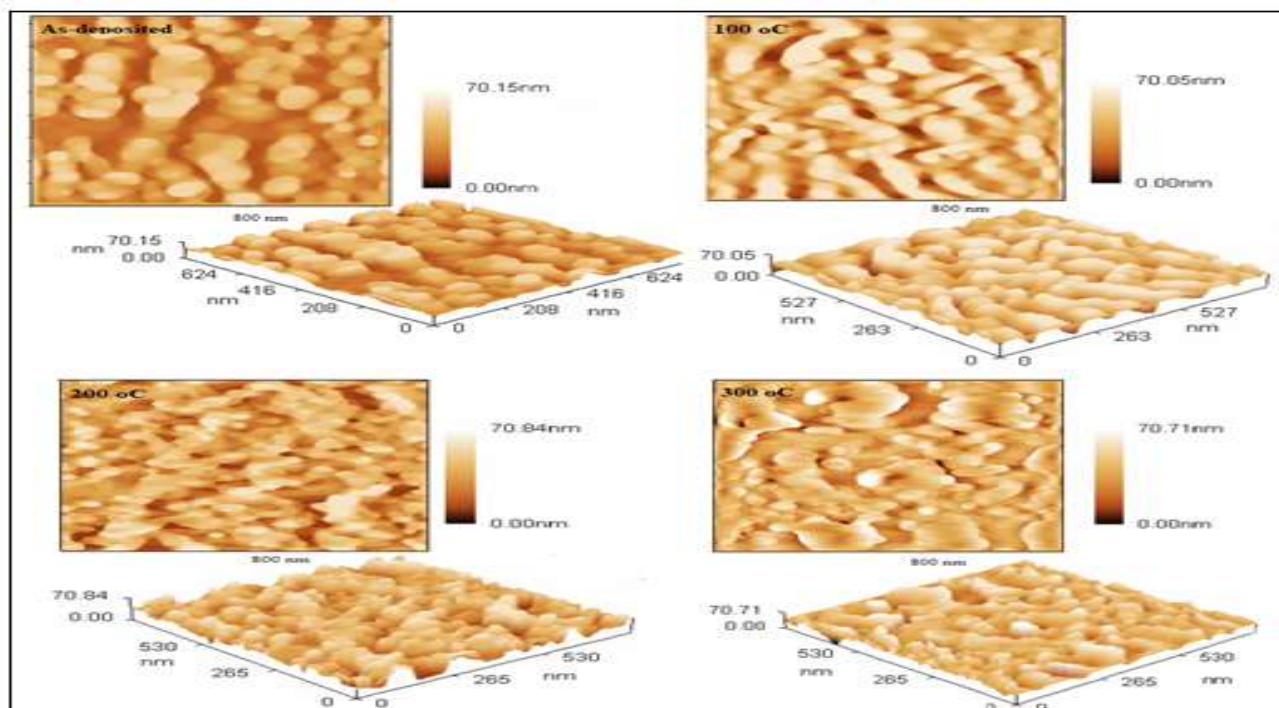
Figure 4: Atomic force microscopy (AFM) images of copper phthalocyanine (CuPc) deposited and treated with different temperatures

Current-voltage (I-V) Characteristics

DC conductivity measurements were carried out using Keithly 2400 semiconductors characterization system. The current-voltage (I-V) characteristics of CuPc films were measured in the direction parallel to the films plane using interdigitated electrode structures. The current–voltage (I-V) characteristics of CuPc thin films before and after heating are shown in the Figure 5.
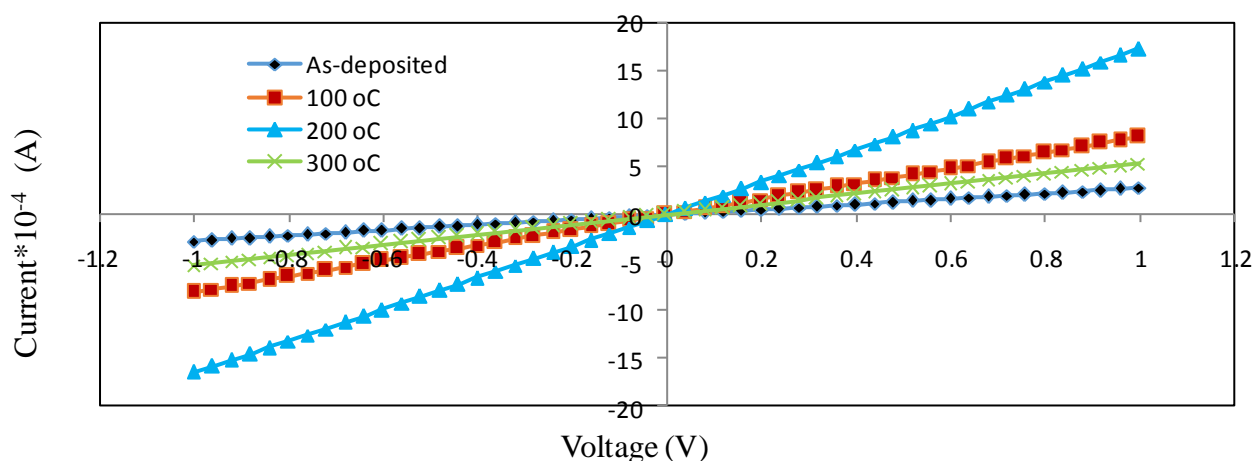

Figure 5: The current–voltage (I–V) characteristics of CuPc thin films at different annealing temperatures

Ammonia Gas Detection

To test the materials in this research we can study the detection from:

The Current-voltage Variation (I-V)

For NH_3 sensing measurements, a constant bias voltage of 1 Volt was applied to the thin film sensors and the dc current was measured. The base line has been taken as the device was exposed to fresh air. The high purity NH_3 stream flowed through the test chamber at room temperature conditions until the electric current reached a steady state value. The variation in electrical current, with and without exposure of NH3 organic gas at a constant applied voltage, has been registered. Figures 6 shows the I-V characteristics of CuPc thin films heated at different annealing temperatures with exposure of organic ammonia gas at different temperature. The dissimilar behavior before and after heat-treatment can be explained by the effect of thermal annealing on the films, which is expected to result in changing the alignment inside the columnar stacking of the molecules in the films [35].
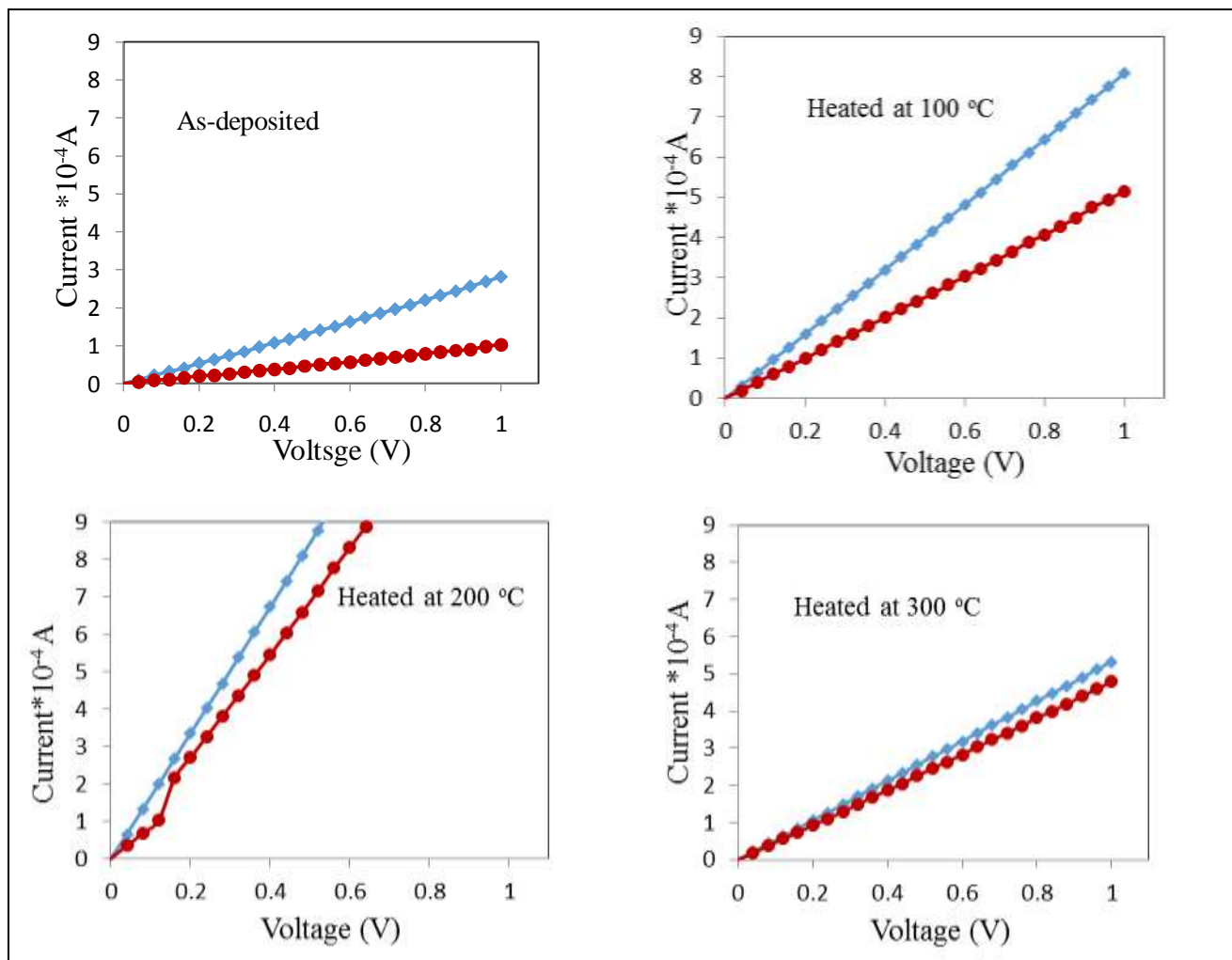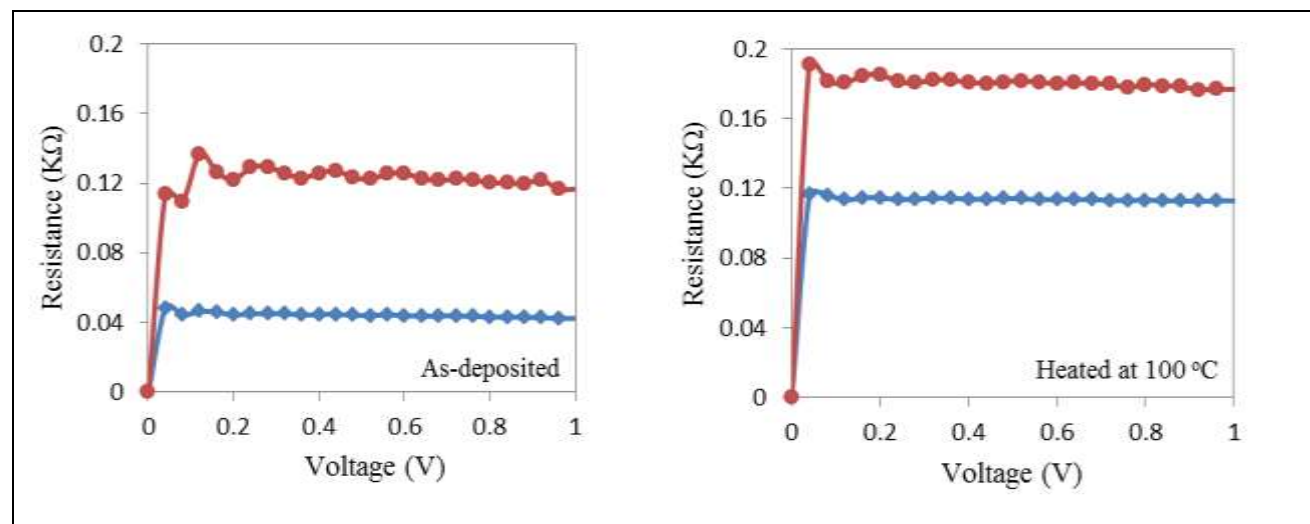
Figure 6: The I–V curves of CuPc thin films before (blue line) and after (red line) exposure to ammonia

The Voltage-resistance Variation (V-R)

Voltage-resistance characteristics (V-R) and the time dependent resistance in a fresh and contaminated air ambient have been investigated to demonstrate the sensor activity of the studied material. All gas sensing measurements have been performed at room temperature and devices were exposed to concentrated NH_3 gas to exhibit the best annealing temperature. Figure 7 represents the V-R curves of CuPc thin films deposited at room temperature and annealed at different temperatures. We observe that the interaction of prepared samples with ammonia gas results in an increase of resistance, which could be due to the reductive nature of ammonia towards strong donors [10].
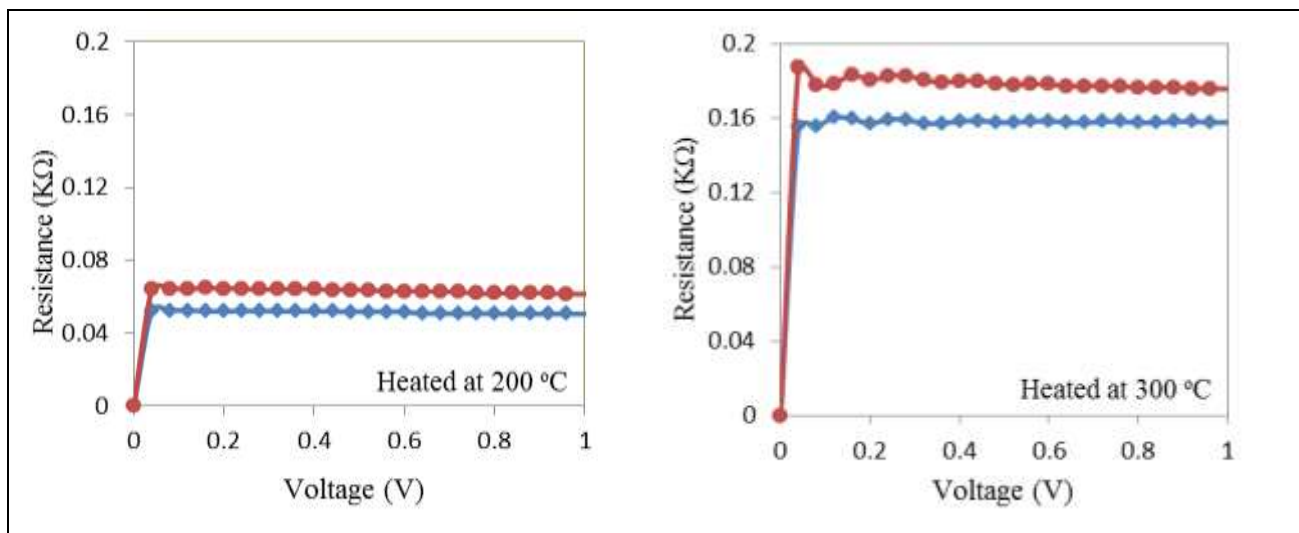
Figure 7: The V-R curves of CuPc thin films before (blue line) and after (red line) exposure to ammonia

The Sensitivity

The sensitivity defined by the following equation [36]:

$$sensitivity = \frac{\Delta R}{R_O} \times 100\% \quad (2)$$

$$\Delta R = R_{gas} - R_O \quad (3)$$

Where R_{gas} and R_O are the resistances of the sensor in test gas and ambient air respectively. Figure 8 represent the change of the sensitivity of the prepared samples verses the annealing temperature. The higher sensitivity was found in the as-deposited films, while the films heated at 300 ºC show lower sensitivity.
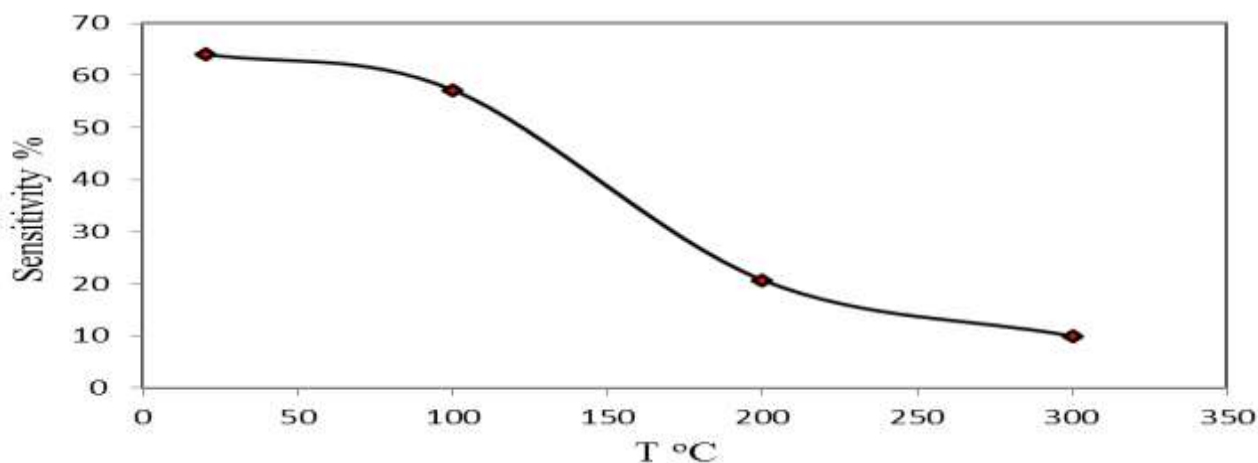

Figure 8: The sensitivity calculated according to eq. 2 for the as-deposited films and heated films at different temperatures

The Resistance-time Dependence Measurements

Time dependency experiment was carried out for all the prepared samples. Only the 100 ºC heated sample showed reasonable results, therefore in this section, the other samples time dependency are ignored. The as-deposited film has shown no-reversibility and this is expected to be due the diffusion of gas molecules in to the sample resulting in irreversible behavior. Figure 9 shows the time dependence experiment for the 100 ºC annealed device. The sensor exhibited very good reversibility after flushing the sample with fresh air immediately, which means that the device shows an excellent recovery time. The response and recovery time which are defined as the time it takes to reach 80% of the steady state and the time required to reach 80% of the base line respectively were measured for the third round and schematically represented in Figure 10.
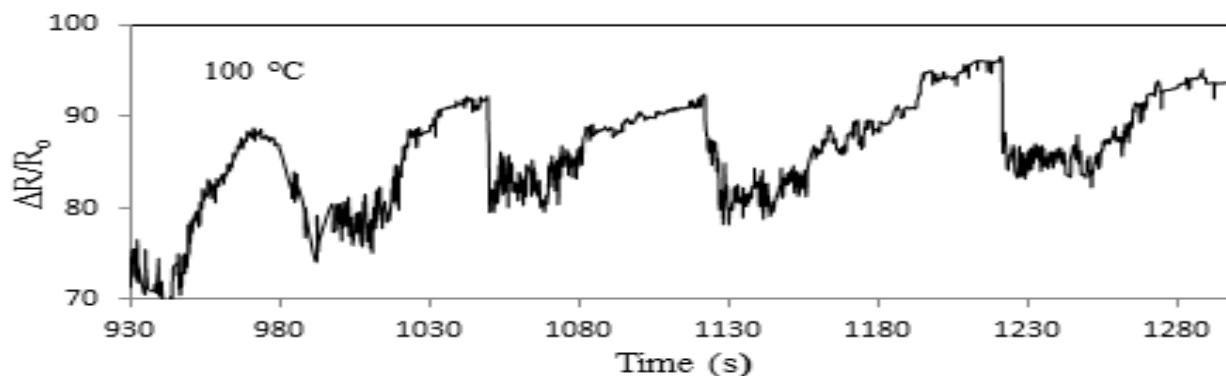
Figure 9: Time dependency of CuPc film at 100 °C upon exposed to concentrated NH₃ gas
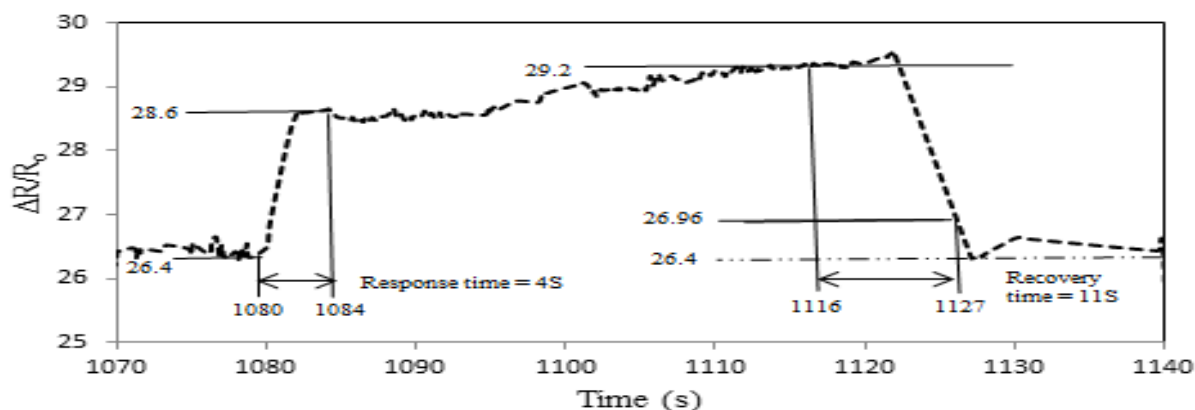

Figure 10: Third round of Figure 9; calculating the response and recovery time

Conclusion

Copper phthalocyanine solution in chloroform was spun onto glass, interdigitated electrodes, and films that were heat treated at different annealing temperatures. The roughness of the films increased at higher temperatures due to preferred unidirectional attachment of the molecules. In the optical spectra, the main absorption bands are broadened after heating through exciton coupling effects which also lead to shifts in the band positions. The optimum sensitivity of the thin films towards ammonia vapor was achieved in the films heated at 100 °C. The response and recovery time of the sensor has found to be 4 and 11s respectively.

Acknowledgments

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