# CuPc based organic–inorganic hetero-junction with Au electrodes

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**Abstract:** A hetero-junction of n-silicon (n-Si) and copper phthalocyanine (CuPc) has been fabricated. The current–voltage characteristics were investigated to explain the rectification and conduction mechanism. The effect of temperature and humidity on the electrical properties of n-Si/CuPc hetero-junction has also been investigated. The characteristics of the junction have been observed to be temperature and humidity dependent, so it is suggested that this junction can be used as a temperature and humidity sensor.

**Key words:** inorganic–organic hetero-junction; n-Si; CuPc
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## 1. Introduction

Very recently, the fabrication and investigation of several organic on inorganic hetero-junctions have been reported[1–7]. These studies have been made owing to their interesting electrical properties and potential applications in electronic and optoelectronic devices such as solar cells, sensors and light emitting diodes. Electrical properties of organic semiconductor devices are dependent on ambient conditions, and this makes them very promising for the development of various types of sensors to evaluate temperature, strains, light, radiation, humidity, etc.[8]. The properties of copper phthalocyanine and other phthalocyanines make them good examples for such usage. Phthalocyanines form a large group of organic semiconductor compounds, which have been the main basis for the search of molecular semiconductors. These materials are most studied and widely used due to their high chemical and thermal stability[9]. Copper phthalocyanine doped by $O_2$ is a p-type organic semiconductor. It is a class of materials that may be deposited as thin films without dissociation and thus, is suitable for the preparation of thin films through thermal deposition. The interfacial properties of CuPc and its variants in their ultra-thin film forms have been studied by Peisert *et al.*[9, 10].

In this work, electrical properties of n-Si/CuPc hetero-junction are investigated at different temperatures. The aim of this work is to investigate and analyze the electrical transport of thermally evaporated CuPc thin film on heavily doped n-Si to determine its essential parameters and electronic conduction properties. It is important to know the parameters of the junction and its characteristics as functions of temperature and humidity for its utilization in an environment where temperature and humidity level changes.

## 2. Experimental

Copper phthalocyanine (Sigma Aldrich) and heavily doped n-silicon wafer with (110) orientation was used for the fabrication of n-Si/CuPc hetero-junction. Au was used for the contacts. The silicon wafer was cleaned using acetone in ultrasonic cleaner at room temperature for 5 min. Then, a low resistivity ohmic contact on the polished side n-type Si wafer was deposited by thermal evaporation of Au, followed by thermal deposition of thin film of CuPc of thickness 30 nm on polished surface by using mask. The contact on CuPc was also made by thermal evaporation of Au. The thickness and area of both contacts was 100 nm and 50 mm$^2$, respectively, while area of inorganic–organic hetero-junction was 125 mm$^2$. All the depositions were made at growth rate of 0.1 nm/s, and vacuum chamber was kept at a pressure of $5.5 \times 10^{-5}$ mbar.

Figure 1 shows the schematic view of fabricated device. Device was also annealed at 200 °C for 15 min and slowly cooled down to room temperature. DC current–voltage characteristics and AC resistances (at 10 and 100 Hz frequencies) were measured in the temperature range of 30–50 °C and at humidity level of 25%–80%, respectively. The temperature dependent current–voltage studies were performed by using a thermo-chuck "Alpha" series system model TP 0315A-TS-2 of Temprotic Corporation USA. It uses a temperature controlled chuck (the thermo-chuck plate platform) as a surface for inducing a localized temperature. Current–voltage measurements on the hetero-junction were done using a KARL SUSS PM5 probe station. The humidity dependent measurements were performed in self made humidity controlled chamber. The CEM DT-8860 digital humidity meter was used for in situ humidity measurements. All current–voltage measurements were taken under steady state conditions. The device immediately gave stabilized output whenever there is change in applied voltage. Keithley 228A voltage source and Keithley

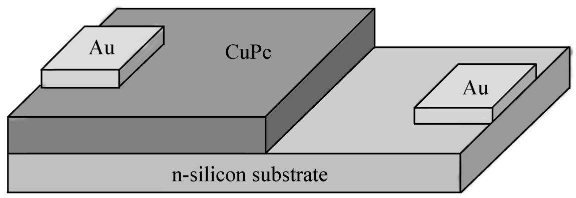


Fig. 1. Schematic view of n-Si/CuPc hetero-junction.

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196 system DMM were used for current–voltage characteristics. Temperature and relative humidity were measured with error of ±1 °C and ±2%, respectively.

## 3. Results and discussion

The forward and reverse biased current–voltage characteristics of the n-Si/CuPc hetero-junction at room temperature are exhibited in Fig. 2 In forward-bias, the CuPc contact was positively biased and the n-Si was negatively biased. The n-Si/CuPc structure represents the inorganic–organic hetero-junction. The behavior of the hetero-junctions is mentioned in Refs. [11–13]. The current–voltage characteristics of the n-Si/CuPc hetero-junction showed rectification behavior which is limited by the magnitude of the energy barrier at the junction interface[14]. The rectification ratio was found 2 at ±3 V. Rectification ratio is the ratio of forward current to reverse current at certain voltage. The thermionic emission over the n-Si/CuPc contact is important at low current density; while at high current density the space charge injection proceed from n-Si into CuPc film, and the current in this case called space charge limited current (SCLC)[11, 13, 15, 16]. The SCLC process physically observed if a concentration of injected (due to the applied voltage and accordingly the created electric field) charges (from junction into dielectric) is larger than intrinsic carrier concentration[17] in dielectric. The injection and transfer of charges in dielectric (in this case in semiconductor) is like to the same processes that take place in vacuum-tube diodes[17]. If $I$–$V$ characteristics obey to square law, $B$ is equal to 2, it is considered no effect of traps. If the $B$ is above of 2, the effect of traps should be taken into consideration.

The behavior of n-Si/CuPc hetero-junction before and after annealing is also shown in Fig. 2. The current–voltage characteristics of the sample before annealing are linear on both forward and reverse biasing while the current–voltage characteristics of annealed sample represent the nonlinear behavior with zero offset current. This behavior may be due to number of factor which may include the reduction in resistivity of copper phthalocyanine film and improvement of film quality. It is also observed from Fig. 2 that the current–voltage characteristics after annealing show asymmetric behavior at low voltage whereas symmetric behavior is seen at higher voltage in both forward and reverse bias. This symmetric response at higher voltage may be due to the narrow depletion layer width at the interface. The biased current ($I$) is nonlinear and is dependent on voltage. This behavior can be explained by the relation[18] as below.

$$I = CV^B, \tag{1}$$

where $C$ is proportionality, and constant $B$ can be determined by

$$B = \frac{\ln I_2 - \ln I_1}{\ln V_2 - \ln V_1}, \tag{2}$$

where $I_1$ and $I_2$ are currents measured at voltages $V_1$ and $V_2$ respectively.

Figure 3 shows the current–voltage characteristics of annealed n-Si/CuPc sample at different temperatures. The temperature dependent electrical characteristics of device were investigated through current–voltage measurements in the temperature range of 30–50 °C. It is observed that the conduction of CuPc thin film deposited from thermal evaporator increases with temperature. The change in characteristics as a function of temperature may be due to the increase in the density of free carriers, either by detraping mechanism[18].

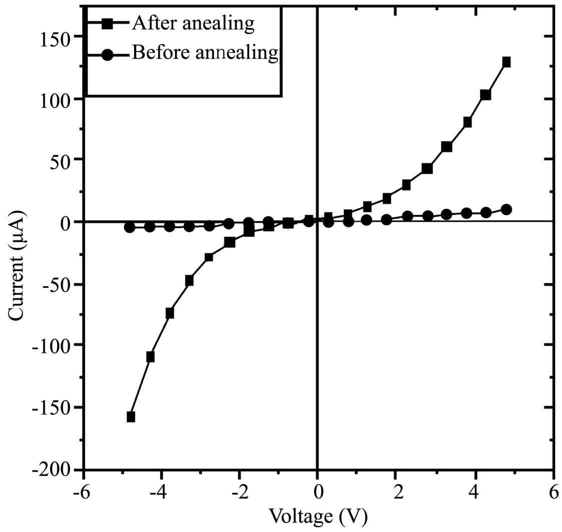


Fig. 2. Current–voltage characteristics of n-Si/CuPc hetero-junction before and after annealing.

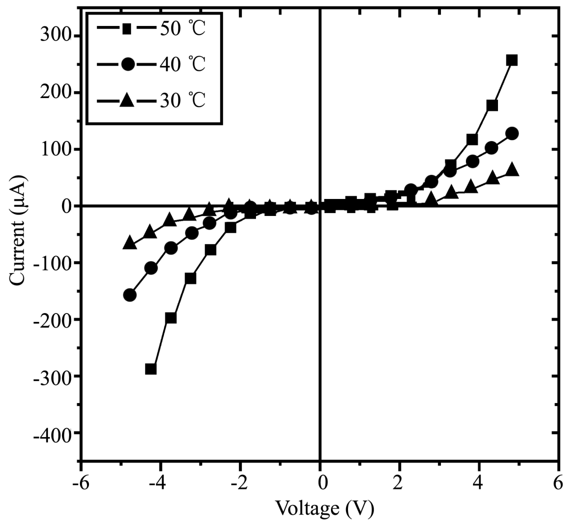


Fig. 3. Current–voltage characteristics of the n-Si/CuPc hetero-junction at 30, 40, and 50 °C.

Figure 4 shows the lg $J$ versus lg $V$ plot of n-Si/CuPc hetero-junction in forward bias at room temperature. It is clear from Fig. 4 that the forward bias characteristics show the three distinct regions separated by transition segments. The region I is an ohmic region with slope about to unity up to transition voltage of about 0.7 V, which obeys the equation $J = q\mu n_o V/d$, where $n_o$ is the concentration of the free charge carriers in the CuPc film, $\mu$ is the mobility of charge carrier in the film, and $d$ is the thickness of the film. The slope of region II is about 2.0 up to a transition voltage of about 1.8 V. This region is also called trapped space charge region. While the region III is called trap free space charge region with the slope value slightly higher than region I. This region shows that, at

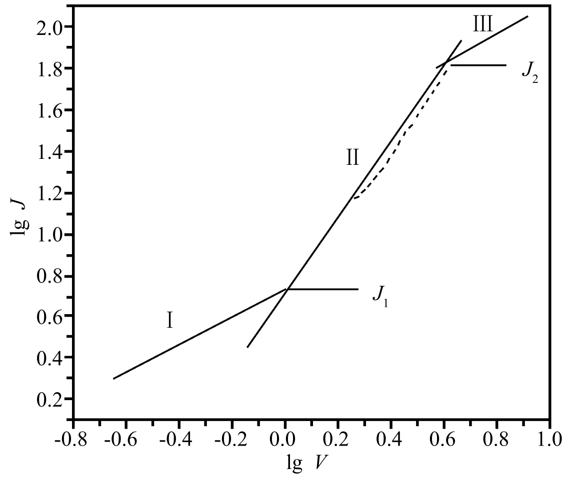


Fig. 4. lg $J$ versus lg $V$ plot of the n-Si/CuPc hetero-junction in forward bias at room temperature.

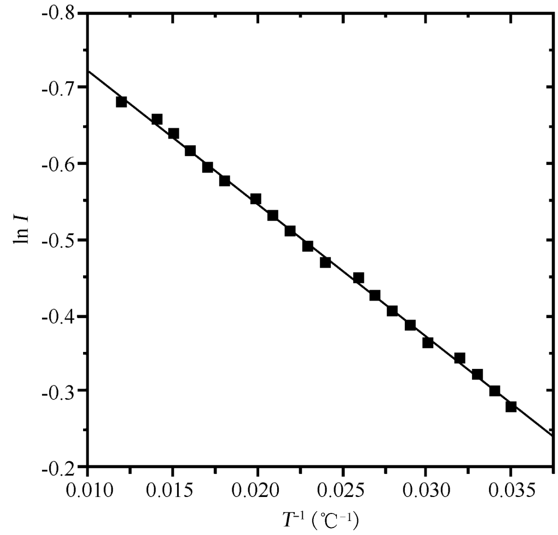


Fig. 5. Plot of ln $I$ as function of $T^{-1}$ at bias voltage of 1.0 V.

higher voltages the slope of the curve decreases because the device approaches the trap filled limit. When the injection level is high the behavior of this region is the same as in trap free SCLC[19–21]. The effective mobility for the device can be estimated by using the relation[18]:

$$J = \frac{9\varepsilon_0 \theta \mu V^2}{8d^3}, \tag{3}$$

where $J$ is the current density, $\mu$ is the mobility, $V$ is the applied voltage, and $d$ is thickness of the film. For p-type organic film, $\theta$ can be expressed as:

$$\theta = \frac{p_o}{p_o + p_t} = \frac{J_1}{J_2}, \tag{4}$$

where $\theta$ is trap factor that is defined as the ratio of free carrier density ($p_o$) to total carrier density ($p_t$ is trapped carrier density). Experimentally, the value of the trap factor can be calculated from the ratio of current density $J_1$ and $J_2$ at the beginning and end of region II, respectively[21]. By using Eqs. (3) and (4), the value of mobility was found to be $10^{-6}$ m$^2$/(V·s).

In Fig. 5, the plot of ln $I$ as function of $T^{-1}$ is shown at a constant bias voltage of 1.0 V. The linear behavior of the plot confirms that, the charge carrier transport is limited by thermionic injection, in agreement with Simmons model[23].

Figure 6 shows the dependence of the device AC resistance on the humidity level. It was measured at room temperature at AC frequencies of 10 Hz and 100 Hz. The graph shows that the resistance drops significantly with the increase of humidity level. The value of slope at 10 Hz is three times the value of slope at 100 Hz. The slope of humidity–capacitance relationship is greater at lower frequencies, showing that the device is more sensitive to humidity at lower frequencies. There may be several reasons for the drop in resistance of the device with elevation of relative humidity level. (1) The decrease in resistance may be due to both electronic and ionic conduction[24]. Ionic conduction exponentially depends on dielectric constant of the thin film material. The absorption of water enhances the ionic conductivity of CuPc thin film due to increase in dielectric constant. (2) At the same time, the disassociation of water

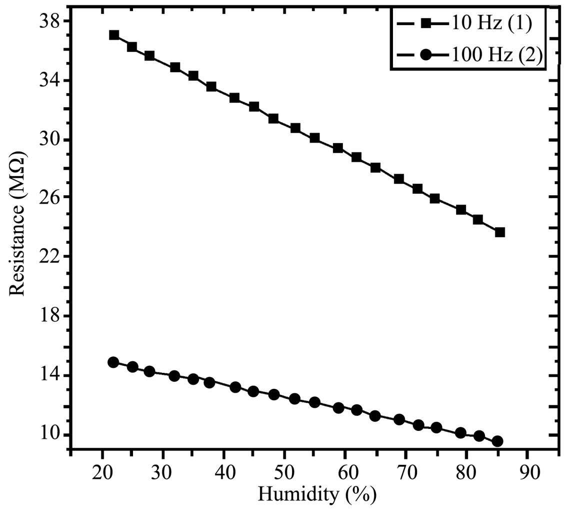


Fig. 6. Change in device resistance as a function of humidity.

molecule into ions may occur that results the decrease in resistance. (3) Polar molecules of water may also decrease the resistance due to increase in proton concentration[25]. (4) There may also be some physical phenomena behind this, such as effect of absorbed water molecule as dipole and impurity[25].

It was found that the effect of moisture on the resistance of the n-Si/CuPc heterojunction was quite reversible. Moreover the resistance–humidity relationships of the samples show good linearity, making it potentially attractive for fabrication of the humidity sensors.

## 4. Conclusions

By thermal evaporation, the hetero-junction of n-Si and CuPc was successfully fabricated. It is observed that CuPc film grown on n-Si substrate showed good adhesion to the substrate. The current–voltage characteristics were analyzed at different temperatures. The CuPc deposited on highly doped n-Si substrate showed the nonlinear current–voltage characteristics. It is observed that the conduction of CuPc thin film deposited from the thermal evaporator increases with temperature and humidity. Due to good humidity and temperature sensitivity, this hetero-junction may be used for a humidity and temperature sensor.

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