

Effect of Cu₂O nano-particles on the temperature sensing and optical switching of poly-(dioctyl-flourene)

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This paper reports the effect of Cu₂O nanoparticles on the temperature sensing properties and optical switching of Poly-(Dioctylfluorene). A surface type capacitive temperature sensor and optical switch has been fabricated by depositing 720 nm thin layer of F8:Cu₂O on pre-patterned silver (Ag) electrodes, using optical lithography and shadow masking followed by vacuum thermal deposition. The effect of temperature on the electrical resistance for sensor and as optical switch by exposing light has been investigated. The sensor responded exponentially with increasing temperature, also exposing to light it work as an optical switch. The on off of this optical switch is will explained by graph. Scanning Electron Microscopy has been employed to study the morphology of F8:Cu₂O thin film. These results demonstrated that the temperature sensor and optical switch made of F8:Cu₂O have excellent accuracy and performance.

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1. Introduction

Up to this time electronic industry has worked on inorganic semiconductors applications because of their useful properties and high stability such as Si, Ge, GaAs etc. and the whole market of electronics is dominant by these materials [1]. The high cost of these materials as well as expensive and complex technology for their device preparation is a big problem [2]. Now the quest has started to discover such alternative materials that have low cost and possess good electrical and optical properties to decrease the end expenditure of electronics appliances and instrumentations. The aforementioned properties have been shown by organic semiconducting materials that have low cost and simple device fabrication technologies [3]. For the first time, in 1950's and early 1960's, electrical conduction in organic materials has been observed when photoconductivity and electroluminescence were noticed in naphthalene and anthracene crystals [4]. In the mid-1960's

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small organic pigments were blended in insulating polymer matrix for xerographic applications [5]. They exhibited semiconducting properties of small organic molecules and mechanical properties of polymers. Since then, a new perspective has been opened on the applicability of organic molecules and semiconducting polymers into electronic and optoelectronic devices [6]. In addition, much industrial application of organic semiconductors may be recognized by investigating their electrical behavior as a function of doping and device fabrication parameters which influence upon the conductivity of these devices [7]. Organic semiconductors that demonstrate alter in their electrical behavior as the ambient conditions changes e.g., radiation, toxic gases and temperature [8].

The electrical properties of some of the organic semiconductors, for example proteins, are dependent upon the ambient humidity level and thus they could be potentially used in the development of humidity sensors [9]. Intrinsic ease connected to the production of organic semiconductor devices relative to inorganic one and dependent of their electrical properties on the ambient circumstances made those very promising for the enlargement of various types of sensors to evaluate temperature, humidity, strain light, radiation, etc. Different researchers reported widely the mean of thermal sensors for different applications [10]. Thermal sensors based on (CMOS) technology utilize the temperature dependent characteristics of MOS transistors for sensing the temperature of the circuit oscillator based designs are one of the most widespread techniques of CMOS based thermal sensors, where the oscillating frequency is converted to temperature readings which depends on temperature [11]. It is self-evident that a sensor's functions is to detect changes (physical, chemical etc.) in the environment [12]. Sensors are utilized in a wide range of applications, including industrial production, process control, environmental monitoring, storage, and agriculture [13]. For low-cost disposable sensors, inorganic semiconductors are not appropriate. Organic semiconductors are one of the most acceptable alternatives to inorganic materials. Organic semiconductors are more appropriate for sensor applications because their physical and chemical properties may be tuned over a wide range of features. Organic semiconductors may be deposited on large flexible substrates at or near room temperature. They seemed promising for use as sensors because of their simplicity of manufacturing, low cost, and environmental sensitivity [14]. In 2008 mahidat, S.Hamilakis *et al.* work on effect of import of additional functional groups on the photocurrent produced by small-molecule organic semiconductors and proved that such synthesis can be applied to even to other active methylene compounds [15].

In 2010 Shufeng, Shuo Li, *et al.* work on humidity sensors based on ZnO colloidal nanocrystal clusters. The ZnO CNCs sensor were found to have high sensitivity and fast response/recovery time to humidity, and their resistance changed approximately three orders of magnitude from about $1.58 \times 10^9 \text{ X}$ in dry air (10 RH%) to $1.65 \times 10^6 \text{ X}$ in 93 RH% air ZnO CNCs sensors were relatively stable to humidity for a long time. [16] In 2014 Nidhi Verma, Satyendra Singh Fabricate an iron titanium oxide thin film and its application as opto-electronic humidity and liquefied petroleum gas which shows maximum sensitivity $4.5 \mu \text{ W}/\% \text{RH}$, which is quite significant for sensor fabrication purposes. The maximum percentage sensor response for LPG was found 2600 which is many folds more than the earlier reported Titania based LPG sensor [17]. In 2014 Peter o and Korner *et al.* made organic memory diodes which can read out 8 current level in a prototype devices via both optical and electrical writing procedure [18]. In 2015 Agus Ismangil, Renan Prasta. *et al* made an automatic switch of LAPAN-IPB Satellite infra-red sensor from lithium tantalite (LiTaO₃) whose sensitivity of this high intensity absorbent for energy and high value of band-gap is great and is therefore potential to be used prospectively for the automatic switch sensor on the satellite platform [19]. In 2014 Kornelia Lewandoska, Agnieszka Podborska *et al.* made an optical signal DE multiplexing and conversion in the fullerene-oligothiophene-CdS system whose peculiar photo electrochemical properties were applied for construction of an optoelectronic logic devices [20].

2. Experimental Work

2.1. Device Fabrication

Figure 1 shows F8 molecular structure for the Ag/F8:Cu₂O /Ag surface type capacitive temperature sensor and optical switch were built using a commercially available microscope glass slide as a substrate. To eliminate the residue, the substrate was first washed in distilled water for 10 minutes before being plasma cleansed for two to three minutes. After plasma cleaning, the 5 micron gap was produced by optical lithography and shadow masking, and the Ag is deposited on it by using Edward Auto 306 thermal evaporator. During electrode deposition, pressure inside the chamber was 1.5×10^{-5} mbar and the deposition rate was 0.2 nm/s. The deposition rate and film thickness were monitored by FTM5 thickness monitor. Poly (9, 9dioctylefluorene) F8 was added to toluene to form its solution and was dissolved using magnetic stirrer and was cooled at room temperature, Cupreous oxide was then added to toluene and was dissolved in using magnetic stirrer and it was also cooled at room temperature, the mass concentration ratio was 10mg F8 and using toluene 1 ml and 10mg Cu₂O in 1 ml toluene as a solvent. Then 5,5ml solutions were taken from both the solution and make a blend. The mass concentration ratio of F8 and Cu₂O was 1, 1 in blend.

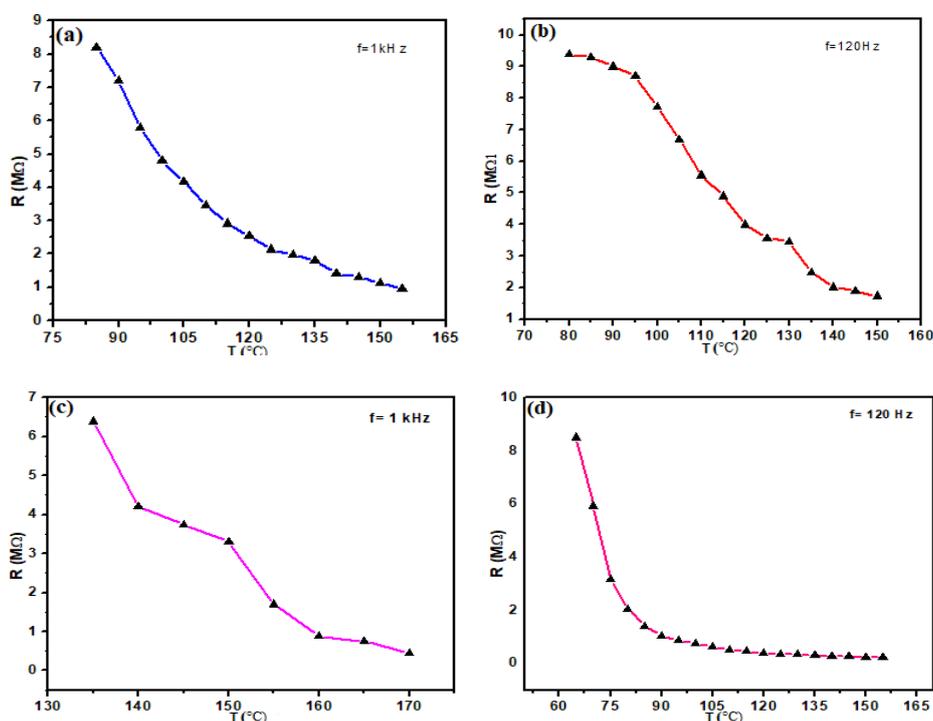


Fig. 1. (a) Temperature response of thin device on 1 kHz (b) Graph of Ag/F8: Cu₂O/Ag temperature sensor at 120 Hz thick sample (c) Response of thin temperature sensor with increase in temperature at 1 kHz (d) Response of temperature sensor with increase in temperature at 120 Hz.

2.2. Measurements

Surface morphology of F8+Cu₂O thin film has been analyzed using Scanning Electron Microscopy. The Energy dispersive spectroscopy (EDS) has been shown. This shows us the elemental analysis of the sample. The EDS of our sample was performed through the SEM For temperature measurements, the Ag/F8:Cu₂O/Ag thin film temperature sensor was placed on hot plate and connected with ESCORTEL-133A LCR meter by crocodile cliff and ohm meter with thermocouple wire is used to check temperature sensing for different values of temperature. The optical switching measurement is carried out by lux meter and LCR meter.

3. Results and discussions

3.1. Device Characterization as Temperature Sensor

The device characterizations were studied by investigating the effects on resistances (R), of the sensor Ag/F8:Cu₂O /Ag, as a function of temperature. The resistances (R) vs. temperature (T) plots are discussed, below, to understand the physics of sensor. In addition, the hysteresis plots will show the recovery of sensor or devices, are also studied. The temperature confidence of the resistance was measured from 80°C to 150°C. It had been observed that resistance decreases exponentially as temperature increases. Ag/F8:Cu₂O/Ag resistive capacitive sensor was sensitive for entire calculated temperature range (80–150°C). Relation between resistivity and temperature was described by following expression

$$\rho = \rho_0 \exp\left(\frac{E}{kT}\right) \quad (1)$$

where in eq. (1) ρ the resistivity at the absolute temperature T and ρ_0 is the pre-exponential factor depends upon T_0 , E is activation energy for conduction and k is Boltzmann's constant. A straight line is drawn between the natural log of conductivity and the reciprocal of absolute temperature, with the slope indicating the activation energy [21, 22].

This is the response of the sensor at 1 kHz which shows us exactly the behavior of the semiconductor F8 as shown in Fig. 1(a). The resistance of the sensor decreases as we increase the temperature. The physics behind this decrease is the HUMO and LOMO gap decreases when we increase the temperature of the device. The relative resistance decrease with the increase in temperature can be explained by taking polarization into account. It is assumed that at higher temperature the numbers of charge carries increase due to polarization by transfer of free charges, so resistance decreases. If we observe the reading taken it shows us that sensor work in a specific range i.e. from 80°C to 155°C, mean this is the sensitive region for this device. Below 80°C and above 155°C the device is not responding significantly. This device will burn if we increase the temperature more and more because of Mott's transition which bring a permanent change in this active blend. It is clear from the first exponential term of the equation 2 that the mobility is temperature dependent.

$$\gamma_{ij} = \gamma_0 f(E_i) \exp\left(-\frac{E_i - E_j}{kT}\right) \exp\left(\frac{2R_{ij}}{a}\right) \quad (2)$$

where f is the Fermi function and γ_0 is a constant that contains an electron-coupling term and the phonon density of states. E_i and E_j are the energy states i and j , respectively, and R_{ij} is the distance between them. Mott develop variable range hopping model [23].

$$\sigma = \sigma_0 \exp\left(-\left(\frac{T_0}{T}\right)^{\frac{1}{4}}\right) \quad (3)$$

where T_0 is the characteristics temperature and its value is given by

$$T_0 = \frac{\beta e^2}{\epsilon k \xi} \quad (4)$$

ϵ is the dielectric constant of the material, k represent Boltzmann constant, ξ the localization radius of the electrons and β a numerical coefficient and its value depends on dimensionality which describes the electron transport at low temperature through exponential distribution of localized states. The model predicts a thermally activated mobility. When temperature is small temperatures, electron transitions occur between states with energies near Fermi level are mainly efficient for transport since filled and empty states with closed energies. This can only be found in this energy range. It is already reported that different fabrication process and different thicknesses of thin film produce different film morphology. The morphology can be carried out by using scanning electron

microscopy (SEM) [24]. It is well known that a physical property strongly depends on surface morphology.

This plot in Fig. 1(b) shows us that the variation occurs in the resistance at 120 Hz, which is more than 1 kHz. This behavior shows us that our fabricated sensor is more sensitive at lower frequency in comparison to higher frequency.

This film of the active material in the sample is thin (.....) and the graph shows that the response is not so good at higher frequency i.e. 1 kHz. As shown in Fig. 1(c). The effect of temperature on the sensor took more time than the thick film device studied in previous graphs, and the variation in resistance is slow.

The graph shows very good response in comparison to previous one. This graph is for small thickness sensor and after 100°C, the graph is nearly straight showing that the device is going towards saturation and the behavior is very good. This graph also shows that our fabricated sensor responded very well to at low frequency i.e. 120 Hz and small thickness as shown in Fig. 1(d).

In this study, we have productively fabricated surface-type Ag/F8:Cu₂O/Ag optical switch and capacitive temperature sensors. The study of the samples of diverse thicknesses shows that the resistance of the sensors decreases with a rise in temperature. In general, such response is credited to reduce in HUMO, LOMO gape due to amplify in temperature which consequences in easy transfer of charge carriers. The sensitivity of Ag/F8:Cu₂O /Ag sensor has been originated to be dependent on the thickness. The experimental results show that the thinner the film, the higher the sensitivity.

3.2. Hysteresis response

The hysteresis responses of this surface type temperature sensor Ag/F8:Cu₂O/Ag makes it an ideal device for temperature sensing ability. The temperature sensing of this device is started from 65°C to 155°C, and then cycled down and different plots are formed for each operating frequency. All 4 hysteries are shown Fig. 2(a), (b), (c) and (d) hysteresis occurs due the difference in path up to some extent. Due to increase in temperature, the HUMO-LOMO gap decreases for the electron due to gain in energy from temperature rise and thus the electron can go easily to conduction band, but when we goes on reverse path i.e. decrease the temperature of the sample slowly and gradually, the gaps between the HUMO and LOMO increases for the electrons due to loss in energy, and thus it takes some time to recover itself back to its original state and thus hysteries is produced.

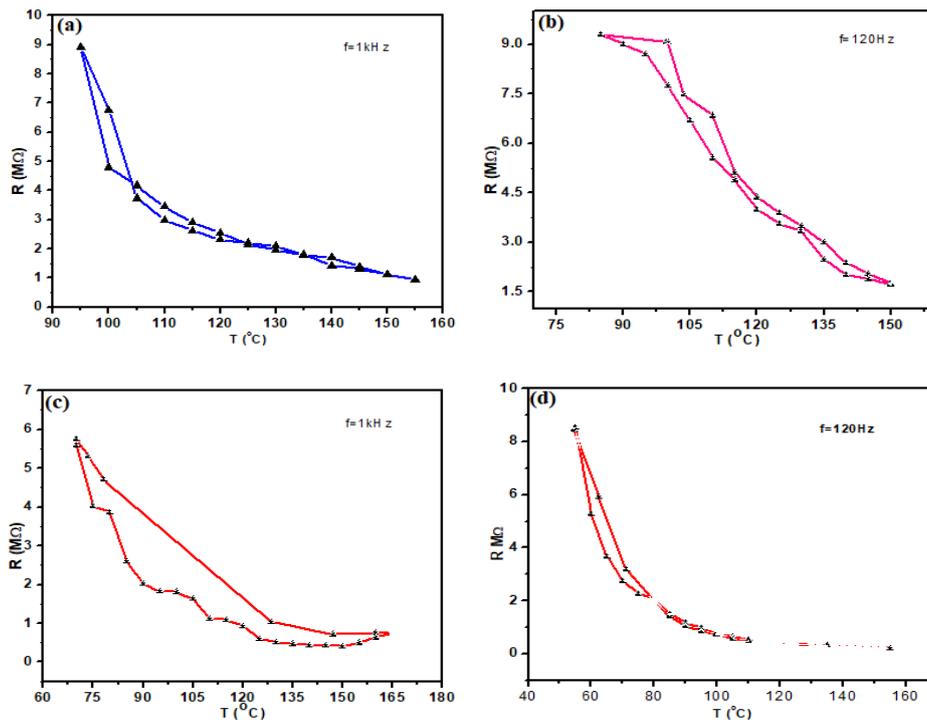


Fig. 2. (a) Hysteresis of thin sample at 1 KHz (b) Hysteresis of thick sample at 120 Hz (c) Response of temperature sensor with increase in temperature at 1 kHz (d) Response of temperature sensor with increase in temperature 120Hz.

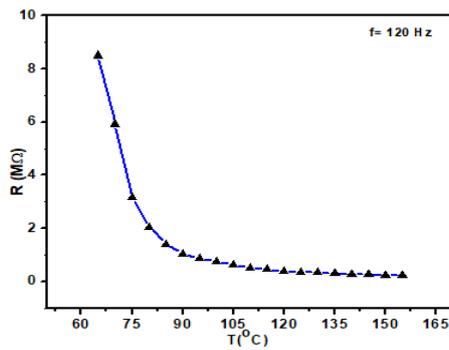


Fig. 3. Response of my temperature sensor on 120Hz.

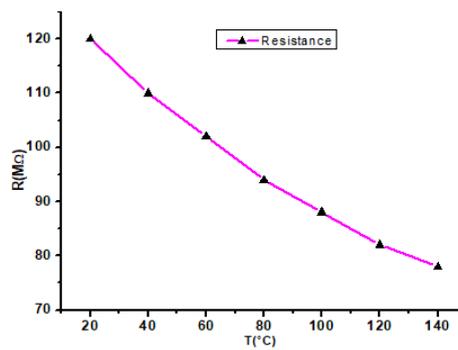


Fig. 4. Fazalurehman temperature sensor.

3.3. Device Characterization as an Optical Switch

In Fig. (5) show the sensor is also characterized for its potential applications as an optical switch. When the sensor was illuminated with light the capacitance is rapidly increased due to optical polarization and becomes saturate after some time. But when light is switched off, again a significant change is observed in the capacitance of the sensor and achieves its initial values. This process is repeated for next cycle to check the reproducibility and repeatability of the sensor which exhibits good consistency.

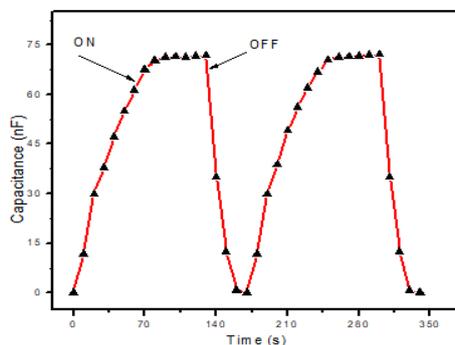


Fig. 5. Optical Switch Repeated cycle to check the reproducibility and repeatability of the Sensor.

3.4. Characterization Technique

The characterization of the thin film of a blend of organic semiconductor polydioctylfluorene + cuprous oxide i.e. F8:Cu₂O cuprous oxide is a nano particle. The material characterization techniques in this chapter are SEM and EDS and have been employed to explore the structural properties of surface type sensor. Now we will give the detail of all above characterization one by one.

3.5. Energy Dispersive Spectroscopy

For the F8:Cu₂O blend, the Energy dispersive spectroscopy (EDS) has been investigated. This shows us the elemental analysis of the sample. The EDS of our sample was performed through the SEM shown in Fig. (7).

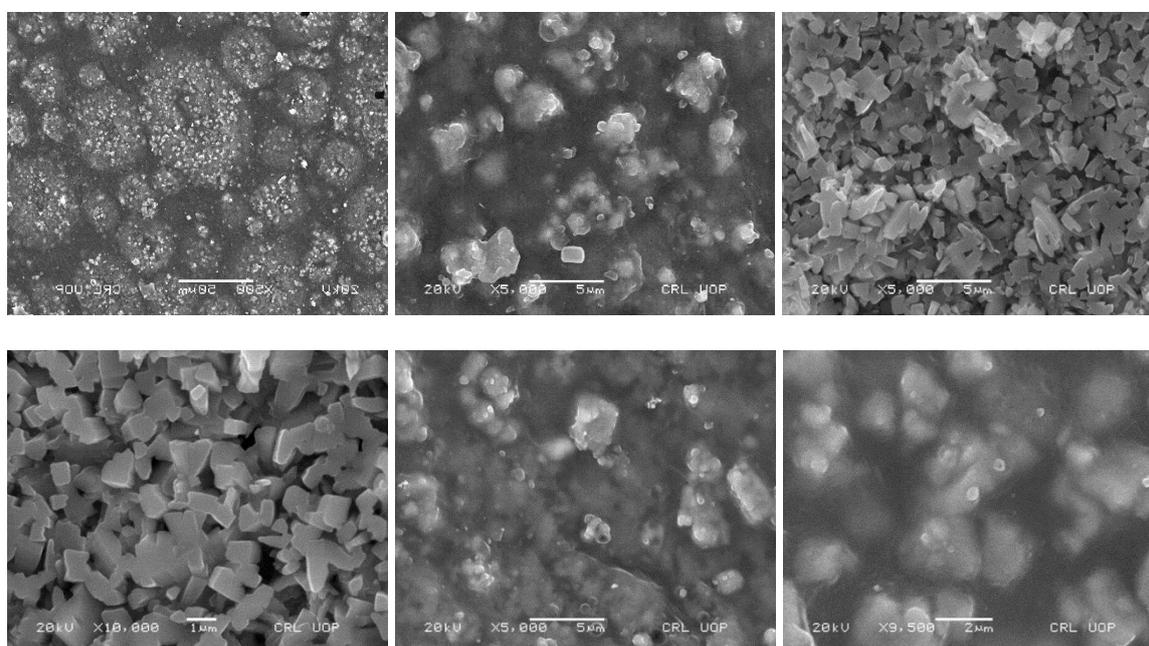


Fig. 6. SEM and EDX images of F8:Cu₂O blend.

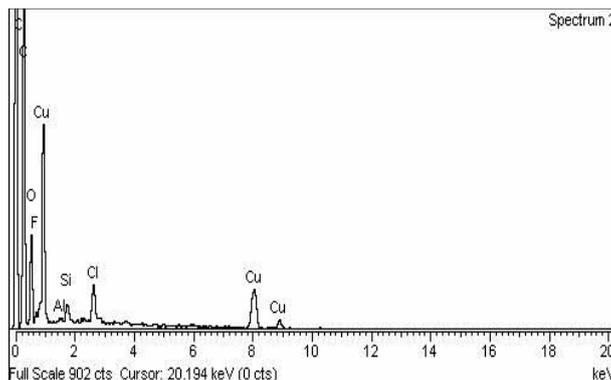


Fig. 7. EDS analysis.

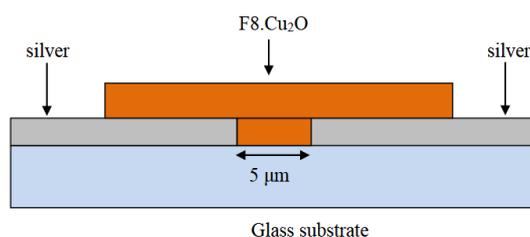


Fig. 8. Device schematic diagrams.

3.6. Scanning Electron Microscope (SEM)

F8 is the organic semiconductor and is soluble in organic solvent i.e. toluene, while Cu₂O is not soluble in toluene because of inorganic nature. In the following SEM image the white dots may show Cu₂O while the black background is F8 in the film form as shown in Fig. (6).

3.7. Comparison of F8 and F8+ Cu₂O as Temperature Sensor

I compare my work with paper whose curve on 120 Hz as temperature sensor, is given [25]. If we compare Ag/F8:Cu₂O/Ag temperature sensor on same frequency, with Ag/F8/Ag so its response is very good because we dope the Cu₂O in F8 and Cu₂O is an inorganic semiconductor. We know that semiconductor behave just like a good conductor as temperature increases. Also due to doping the band gap of F8 decreases and conduction increases because on little amount of potential difference supplied electrons can go from valence band to conduction band. Also we can say that by doping Cu₂O the band gap decreases due to increase in charge carrier. The behavior of Ag/F8:Cu₂O/Ag temperature sensor on 120Hz is as under. This shows the behavior of good semiconductor, as we observed from graph very soon its resistance decreases as compare to above one as shown in Fig. (3) and Fig. (4).

4. Conclusion

In this research work, Ag/F8:Cu₂O/Ag surface type sensor was fabricated by one of the simplest techniques, the drop casting technique and characterized from dissimilar angles, i.e. SEM, EDS, a variety of sensing parameters such as the effects on resistances (R) of the sensor Ag/F8:Cu₂O /Ag were studied as a function of temperature. The resistance R and temperature C⁰ was plot at two diverse frequencies, i.e. 120 Hz and 1 kHz. It was found that the receptive regions are different for different material.

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