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Orange Dye Thin Film Resistive Hygrometers

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Abstract

An investigation on electrical properties of organic semiconductor, Orange Dye (OD), $C_{17}H_{17}N_5O_2$, resistive hygrometers was made in present study. Organic thin films were deposited on substrate by different thin film deposition methods, such as by vacuum evaporation method (Aluminum/Orange Dye/Aluminum), by spin-coater method from solution (Gold/Orange Dye/Gold), and in normal gravity condition by placing drops of OD solutions over the surface of tissue paper (Tin metal/Orange Dye in tissue paper/Net metal). As OD is also temperature sensitive, that is why to compensate temperature effect for the measurement of humidity dependent electrical properties, special arrangement was provided over the same substrate, but encapsulated from humidity environment.

The AC (frequency of 10 Hz) and DC resistances were evaluated from current-voltage characteristics of all samples of resistive hygrometers, measured in the temperature interval range of 20-70°C and relative humidity range of 30-80%. It was observed that the resistance of the OD decreases with a rise in temperature. Similarly, OD resistance is observed to decrease with increase in humidity level. The relative resistance ratio to relative humidity was found 30 and 12 for the samples deposited by vacuum evaporation and from solution by spin coater respectively. Humidity dependent on electrical properties of these resistive hygrometer make them attractive for use in development of industrial humidity meters.

Introduction

Organic semiconductor materials based devices have been the subjects of intensive investigation in the past few years due to their low cost, simplicity of devices fabrication, and interesting electrical and optical properties. Many potential applications of organic semiconductors may be realized via investigation and modification of their conductivity [1-4]. Presently some of organic semiconductors are used in commercially produced light emitting diodes. Some of organic semiconductors are very sensitive to humidity [1,2], temperature [5,6], IR, visible and UV radiation [7], and different types of gases such as ammonia [8]. Therefore, investigation of conductivity of organic semiconductors under different conditions is very promising field for development of various sensors for humidity, temperature, light, radiation, strain, gases, *etc*. Undoubtedly, organic semiconductors will find more niches among the electronic materials in the near future.

At present time in resistive hygrometers, the most common material that is used is lithium chloride [9, 10]. The mixture of lithium chloride and carbon is put on insulating substrate between metal electrodes and forms bulk type sensor. Resistance of the element decreased with increase of humidity, it may be due to the formation of some energetic disorder in the element. Resistance of the hygrometer should be measured by applying AC to Wheatstone bridge or by combination of current and voltage measurements [9,10]. DC voltage is not applied because it tends to breakdown the lithium chloride to its lithium and chlorine atoms. The resistive hygrometer must be operated either in constant temperature environment or temperature corrections must be incorporated. Response times are typically of the order of a few seconds [9, 10]. Resistance of hygrometer changes from 10 kΩ to 10^3 MΩ as humidity changes from 100% to 0%.

The orange dyes (OD) as a *p*-type organic semiconductor have potentially application for electronic devices. In earlier works [11] a two-layer structure, poly-N-epoxipropylcarbazole/OD heterojunction, deposited from solution at high gravity conditions

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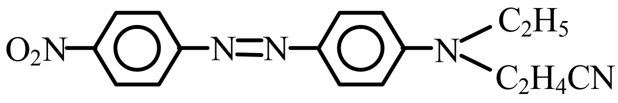
by centrifugation has shown a rectification behaviour. On the other hand, vapour deposition technology is used widely for fabrication and investigation of thin film organic devices [1,2]. This being low temperature (400-600°C) process, allows growing thinner and more uniform films. It is known that the structures and the properties of organic semiconductors are highly dependent on the fabrication technology. Generally, organic materials have large molecular weight, strong intramolecular and weak Van der Waal's intermolecular bonding. To optimize the structural properties, which define the electrical behaviour of the device different thin films deposition techniques, are commonly employed with variable processing parameters. Thus, it is assumed that a suitable processing technology may result in a better electrical performance of finished device from a given organic material [12].

In this article, electrical properties of organic semiconductor orange dye resistive hygrometer, deposited by vacuum evaporation, spin coater from solution and in normal gravity conditions as well, as a function of humidity ranging from 30-80% were reported.

Device Fabrication

The molecular structure of organic semiconductor orange dye (OD), $C_{17}H_{17}N_5O_2$, is shown in Fig. 1. Molecular weight of OD was 323 g/mole and density was equal to 0.9 g/cm^3. By "hot-probe" method, it was found that material was *p*-type semiconductor. The thin films were obtained by thermal evaporation in a high vacuum environment with typical background pressure of 10^5-10^6 mbar. The material OD was loaded in a crucible, in the form of pellet, which were resistively heated. The temperature of the sample holder could be controlled in the temperature range of 500°C by resistive heating elements and water-cooling. First of all the metallic (Al) films were growing on the surface of thermally stable glass substrate. After this, the semiconductor orange dye film was grown on the metallic electrodes. The deposition rate was monitored by some quartz crystal and maintained from 4 to 8 Å/s. After evaporation the substrate was rapidly cooled to room temperature in order to prevent excessive desorption from the substrate. The thickness of the films was monitored insitue with a quartz crystal oscillator and was found approximately 4000 Å. Figure 2 shows cross-sectional view of this surface type device. In the device, the gap between metallic electrodes was equal to 0.15 mm with length approximately 4 cm.



OD

Fig. 1. Molecular structure of orange nitrogen dye (OD).

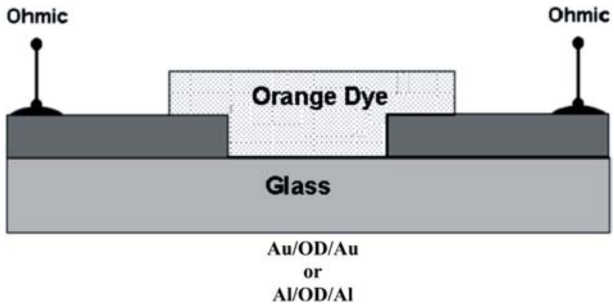


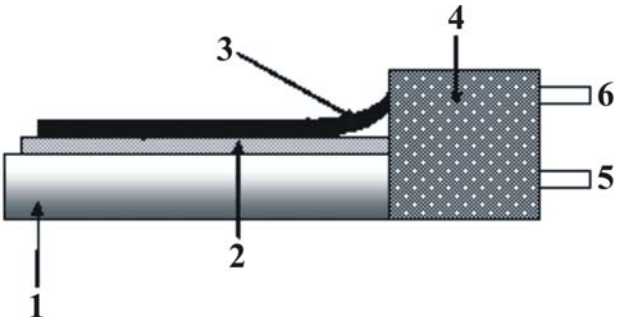
Fig. 2. Cross-sectional view of Au/OD/Au and Al/OD/Al samples.

For other surface type sample, thin films of gold (Au) were deposited over the surface of thermally stable glass substrate by cathode sputtering as an electrode for external electrical connection. The films were deposited from the 10 wt.% solution in distilled water of OD at normal gravity conditions of 1 *g*, where *g* is acceleration due to gravity, at room temperature by using a spin coater rotating with angular speeds of 1000 rpm. This surface type sample was fabricated by dropping 0.05 mL to 0.10 mL of 10 wt.% solution of OD over the surface of gold thin film on glass substrate. The OD film on the substrate was approximately 6-8 mm in diameter. Distance between gold electrodes was found 0.03 mm with length of electrodes about 6-8 mm. The thickness (d) of the OD thin film was estimated via the mass (m), density (ρ) and area (A) of deposited film by the following expression:

$$d = m/A\rho \tag{1}$$

(as the volume (V) of the OD film is equal to $Ad = m/\rho$) and it was found approx 0.1 mm. Optical examination showed that the films grown were homogeneous with mosaic like texture.

The last one, sandwich type sample, of tinned metal/OD in tissue paper/net metal (TM/OD/NM) was fabricated as shown in Fig. 3. In this sample, the tissue papers were wetted by drops of OD solution in distilled water and placed onto the surface of tin metal as substrate as well as electrode. The thickness of the tissue paper estimated by optical microscope was equal to 0.1 mm. Another electrode of net metal was placed over the surface of wet tissue paper, which allows the penetration of water molecule to the OD saturated tissue paper.



Samples: 1 – tinned metal substrate (electrode), 2 – OD in tissue paper, 3 – net metal electrode, 4 – dielectric holder, 5 and 6 – terminals.

Fig. 3. Schematic diagram of tinned metal/OD in tissue paper/net metal (TM/OD/NM)

As OD thin film is also sensitive to temperature effects in order to compensate this effects to humidity measurements, a temperature sensor was provided over the same substrate at which humidity hygrometer were fabricated as shown in Fig. 4 for the case of surface type sensors. The temperature sensor was made from another OD thin film on the same substrate. However, in order to prevent effect of humidity, the temperature sensor was encapsulated.

I-V characteristics were evaluated by using a DC/AC measurement station with temperature adjusting facility. The measurements were carried out in the temperature and humidity range 20 to 60°C and 30-80% RH respectively, with an experimental temperature and humidity measurement error of ±0.5°C and ±3% RH respectively.

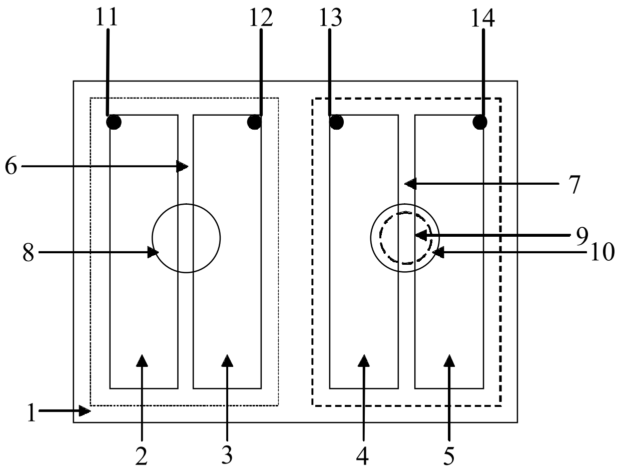


Fig. 4. Schematic top view of hybride resistive hygrometer: (1) glass substrate, (2, 3, 4, 5) gold or aluminum films, (6, 7) gaps, (8, 9) orange dye, (10) capsule, (11, 12) terminals of humidity sensor, (13, 14) terminals of temperature sensor.

Results and Discussion

Figure 5 shows dependence of vacuum-deposited Al/OD/Al surface type sample's resistance on humidity at room temperature. The characteristics showed that resistance drops strongly with increase of humidity. The initial average drop rate (% change in resistance per unit change in humidity) is equal to 30. Sensitivity of OD to humidity is sufficiently large. Therefore, it is expected that OD may be used in humidity meters to replace lithium chloride [9,10]. As the resistance-humidity relationship is nonlinear; therefore, linearization circuit (that usually applied in instrumentation devices particularly with nonlinear sensors) is required to make them linear. The large increase of conductivity of OD with humidity may be due to both ionic and electronic conduction. In particular, ionic conduction exponentially depends on dielectric constant of thin film medium [13]. The absorption of water, which has a relatively high dielectric constant, may generally enhance the ionic conduction of OD. At the same time due to the correlation of OD and water molecules, the dissociation of water molecules into ions may occur that results the increase of conductivity of the matter. On the other hand, polar molecules of water may increase concentration of holes and conduction in OD thin film semiconductor. In order to clear the physical phenomena behind the scene, further detailed investigations are required.

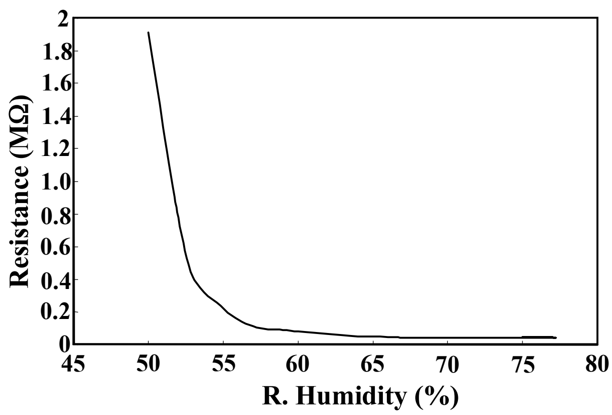


Fig. 5. Dependence of the Al/OD/Al sample's resistance on humidity.

Figure 6 shows the resistance (impedance) – humidity relationship of the deposited thin film surface type resistive hygrometer (Au/OD/Au) from solution, measured at room temperature. Sample 1 was made by placing one drop of approximate volume of 0.075 mL of OD solution. While, sample 2 was made by placing three drops in sequence of approximate total volume of 0.22 mL of OD solution onto the surface of gold. Experiments were performed in both DC and AC (10 Hz), as applied power sources. It is concluded from the Figure, that the resistance (or impedance) drops were 4 to 5 orders of magnitude from 10^3 MΩ to 10 kΩ in humidity range of 40-70%. Sample 3 is same as sample 2, but measurement is performed with AC applied source. From Figure 6, it is clear that both DC and AC measurements of sample 2 are very close to each other. The relative change of resistance per unit change in relative humidity is found to approximately equal to 12. It is further observed that response time of resistive hygrometer was found from 1 to 3 seconds approximately. For the sandwich type tinned metal/OD in tissue paper/net metal (TM/OD/NM) sample it was found actually the same character of resistance – humidity behaviour as it was observed for the (Au/OD/Au) one.

Figure 7 shows voltage-current characteristics of the resistive hygrometer (for the sample 2) measured at room temperature and 42% RH. It is seen that characteristics are quasi-linear.

Figure 8 shows impedance-temperature relationship of OD thin film deposited from solution and encapsulated as surface type Au/OD/Au sample (it is shown as thermistor in Fig. 4). Temperature resistance coefficient of the sample was found equal to –3.0%(°C)$^{-1}$ at 40°C. This is typical value for most organic semiconductors [1,2]. Though humidity dependence measurement of OD based devices is larger than temperature dependence measurement in several orders of magnitude, for accurate humidity measurement, temperature compensation arrangement is essentially employed into the resistive hygrometers.

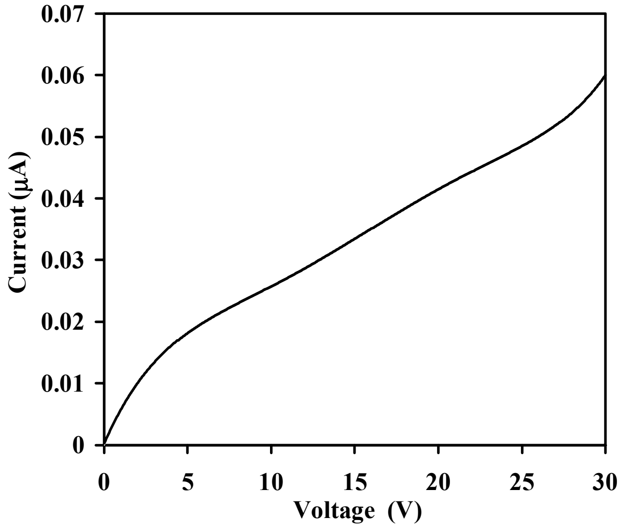


Fig. 7. Voltage-current characteristics of the Au/OD/Au resistive hygrometer (sample 2) at humidity 42%.

Conclusions

Organic semiconductor Orange Dye (OD) based thin film resistive hygrometers were fabricated by

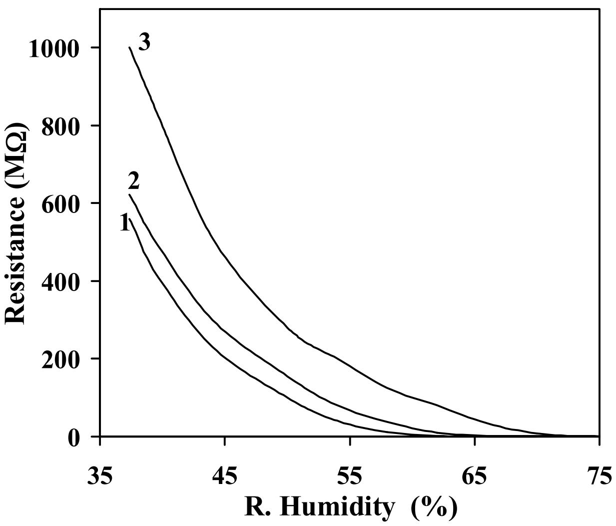


Fig. 6. Dependence of the Au/OD/Au samples' resistances on humidity: 1 – sensor No 2 (in AC, 10 Hz), 2 – sensor No 2 (in DC), 3 – sensor No 1 (in DC).

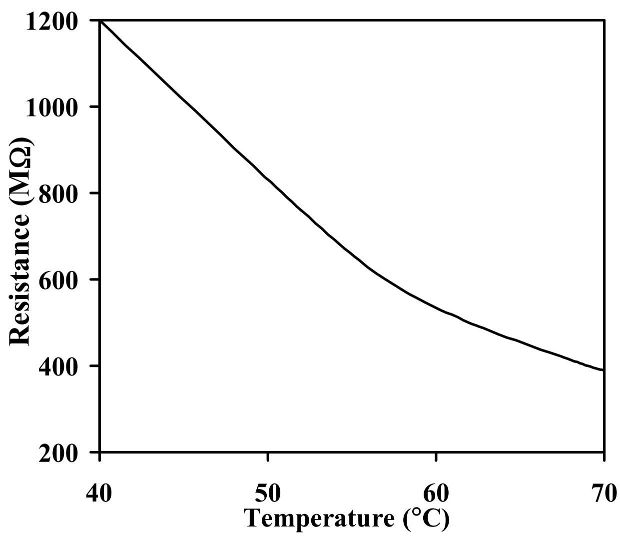


Fig. 8. Resistance-temperature relationship of encapsulated Au/OD/Au sample.

different deposition methods such as by vacuum evaporation, by spin coater from solution and by normal gravity deposition of solution at room temperature. It was observed that the grown organic thin films were uniformly spread over the substrate, when films were deposited by vacuum evaporation and by spin coater. All thin OD films samples, deposited by any method, showed good adhesiveness over the target surface.

Resistance-humidity relationships of these hygrometers were evaluated at different humidity conditions. It was observed that all samples of resistive hygrometers either of surface type structures Al/OD/Al fabricated by vacuum evaporation deposition method or Au/OD/Au fabricated by spin coater deposition method from solution or the sandwich type tinned metal/OD in tissue paper/net metal (TM/OD/NM) sample, showed humidity dependent electrical properties. The changed characteristic as a function of humidity may be associated to the increase in the number density of ions in the device. It may be due to either by the absorption of water, which generally enhances the ionic conduction of OD, or may be due to the some structural changes of OD with water molecules, which cause dissociation of water molecules into ions in material and increase of conductivity of the OD. Resistance-humidity relationships of the samples are non-linear. However, at low humidity values this relationship is relatively sharp. As OD is also temperature sensitive, therefore, in order to compensate temperature effect for the measurement of humidity dependent electrical properties, special arrangements were provided over the same substrate, but encapsulated from humidity environment. Humidity dependent electrical properties of these resistive hygrometers make them suitable for industrial humidity meters.

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