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# Chemiresistive electrical properties of chloroaluminum phthalocyanine nanostructured thin films

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Electrical properties of chloroaluminum phthalocyanine (ClAlPc) were investigated as a function of chemical environments. ClAlPc thin films were deposited onto interdigitated gold electrodes by thermal evaporation method with a thickness about 200 nm. The field emission scanning electron microscopy (FESEM) image showed ClAlPc nanosized particles (50- 80 nm) and X-ray diffraction confirmed that the thin films are in α-phase structure. Electrical measurements demonstrated that the semiconducting and photoconducting properties of ClAlPc thin films are influenced by working temperature and chemical environments. The sensitivity of devices versus humidity, ammonia and ethanol has been investigated as function of analyte concentration and working temperature. Devices were also used as chemiresistive sensors in chemical environments and it was found that devices can be also calibrated as humidity-selective sensor with respect to chemical vapor concentration at room temperature. Finally, long-time stability of devices was also investigated for a period of time and obtained results showed that the stability of devices is optimum in dry air in comparison with other environments.

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*Keywords:* Chloro-aluminum phthalocyanine, Electrical properties, Chemical environments, Humidity sensor, Chemiresistor

## 1. Introduction

Organic semiconductor devices have enjoyed increasing interest because of their potential low cost applications, easy processing, great opportunity to modify their chemical structures and good compatibility with a variety of substrates. Phthalocyanines (Pcs) are a robust class of semiconducting organic small molecules and there is a growing interest in study of them based on their good thermal and chemical stabilities, simple and versatile alternative to fabricate thin film devices. Phthalocyanine nanostructures have been proposed to be used as various applications including chemical sensing [1- 3], solar cells [4], photovoltaic [5, 6], nonlinear optics [7] and photoelectronic [8, 9]. Phthalocyanines include conjugated $\pi$-electron systems with 18 $\pi$-electrons in their skeletal structures, it enables the electrons to de-localize throughout the whole system and thus many atoms may share them. The de-localized electrons may move around the whole system and become the charge carriers to make them conductive. Most of the phthalocyanines are p-type organic semiconductors, phthalocyanine thin films can be prepared by different physical and chemical synthesis techniques; thermal evaporation is one of these methods to prepared Phthalocyanines thin films. Electrical properties of phthalocyanine nanostructured thin films have been studied in different works [10- 12] which confirm that the electrical properties of Pcs are functions of various factors such as substrate temperature [13], post-deposition annealing [10], chemical environments [14].

Metal-phthalocyanines (MPc), thanks to skills such as great processability, stability and rich substitution chemistry are one of the best candidates for novel molecular electronic devices [15]. Halogenated phthalocyanines are the other kind of phthalocyanines [2, 16], which are used to fabricate semiconductor devices. Phthalocyanines are also used as sensitive materials to fabricate gas and humidity sensors [17- 19], and the electrical measurements can be carried out either using planar or sandwich devices. Planar devices consist of an active thin film, which is coated over a planar interdigitated electrode, and use as gas sensors by DC electrical characteristics, the electrical resistance change of the sensing material is usually measured as the output. The sandwich configuration is used in thin film diodes and transistors [2, 15]. Sandwich devices can be also used as gas sensor; the sensitivity of this kind of devices can be controlled by thickness of thin films [20]. Single layer and heterojunction sandwich devices can be fabricated by phthalocyanines, metal|Pc and Pc|Pc junctions have been studied in some works [2, 20, 21]. Gas sensors are operated by different mechanisms, which can be divided into two main categories based on chemical and physical behaviors of the sensing materials. IUPAC’s report [22] and Chen’s review [23] are two important literatures for classification of gas and humidity sensors and configuration of different sensors. In our laboratory, extensive studies were carried out by using of chloroaluminum phthalocyanine (CIAlPc) thin films as an active film to fabricate humidity sensor. DC electrical properties of CIAlPc planar devices were obtained in different chemical environments and the sensitivity of devices versus relative humidity was tested. In present study, we also studied the effect of ammonia and ethanol vapors as chemical environments on sensitivity of devices versus humidity.

## 2. Experimental

Chloro-aluminum-phthalocyanine (ClAlPc) in powder form was synthesized in our laboratory as reported [16]. Interdigitated gold electrodes with a 100 µm gap were fabricated photolithographically on pre-cleaned polyborosilicate glass (washed sequentially with toluene, carbon tetrachloride and acetone) with a dimension of 8 mm × 8 mm as substrate. ClAlPc was thermally evaporated over the electrode arrays with a thickness about 200 nm; the thickness of thin films was monitored during deposition by using a quartz crystal monitor, depositions were carried out using molybdenum boat in vacuum at a pressure of $10^{-5}$ mbar. The substrate temperature and deposition rate were controlled at 25ºC and 0.5–1.0 Å/s, respectively. ClAlPc was also deposited on glass substrate in the same process of devices fabrication to study the surface morphology of ClAlPc nanostructured films. The surface morphology and crystal structure of ClAlPc thin films were characterized using a field emission scanning electron microscopy (FESEM- Philips, XL3, Netherland) and a X-ray diffractometer (XRD- Eqinox 300, Cu Kα radiation, France)

The electrical and sensing properties of the devices were monitored by continuously recording current and resistance of samples at variable and constant potential using a stabilized DC power supply and an electrometer (Keithley 200). Electrical measurements were carried out in dark and light conditions at different temperatures and the effect of chemical environments (humidity, ethanol and ammonia) on conductivity of devices was also obtained. The diluted vapors with high purity $N_2$ were passed through the test chamber at a flow rate of 500 ml/min and controlled by a mass flow controller and gas sensitive electrical properties of ClAlPc thin films were examined as a function of chemical vapors concentration. The sensitivity, reversibility and response of devices versus humidity were obtained in different chemical environments.

## 3. Results and discussion

### 3.1 Structural characteristics

The X-ray diffraction (XRD) pattern of ClAlPc thin film, deposited on glass substrate at room temperature, is shown in Fig. 1a. A single peak (2θ = 6.83°), which can be identified as the (200) plane of α-phase structure, is observed at room temperature and the lattice spacing was obtained (d = 12.88 ˚A). The peak intensity of ClAlPc in the present study is smaller than that reported in our previous literature [2], which is interpreted as the low crystallization of ClAlPc based on the rate of deposition and morphology of substrate. Fig. 1b shows the surface morphology of ClAlPc nanostructured thin film deposited on polyborosilicate glass substrate (in the same process of devices fabrication) at room temperature. The FESEM image confirms that the nanosized particles are spherical in shape with a grain size of 50–80 nm, the distribution of the nanoparticles is almost the same throughout the whole surface. Nanoparticles with large ratio of surface area (A) to volume (V) can enhance the response of devices to environmental changes.

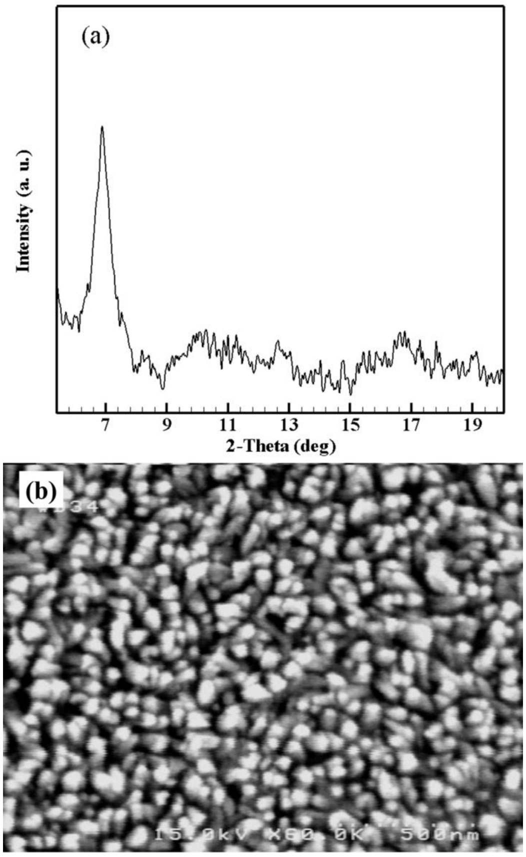

*Fig. 1. (a) XRD pattern and (b) FESEM image of ClAlPc nanoparticles deposited on glass substrate.*

### 3.2 Electrical measurements

Freshly evaporated devices were kept in the vacuum chamber at a fixed bias (12 V) for a period of 24 h, after that a mixture of zero grade air and 20% oxygen was introduced into the chamber for a period of time and thin films were doped by $O_2$ and the influence of $O_2$ dopants on conductivity of thin films was recorded over the period. As shown in Fig. 2, there is a rapid decrease in dark current during the first 75 min followed by slower increase, which continues for the whole period. The reason for the initial drop may be associated surface cleansing process whereby the initial exposure to oxygen generates volatile surface species [24]. ClAlPc can be treated as a p-type semiconductor due to doping by oxygen, $O_2$ molecules act as impurity in the extrinsic conduction region. The formation of charge-transfer complexes at the surface of ClAlPc film leads to $ClAlPc^{+}O_2^{-}$ formation and injection hole charge carriers near the surface of thin films [25].

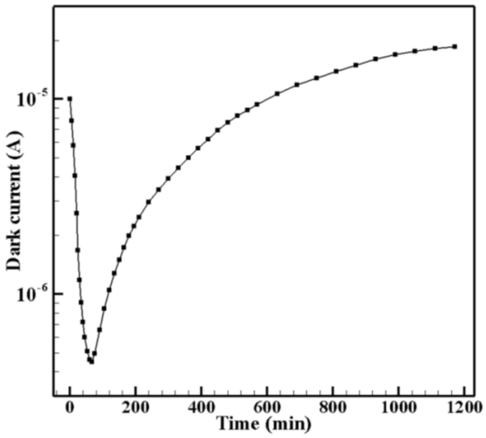

*Fig. 2. Dark current measurement of a device at zero grade air (20% $O_2$).*

The dark current–voltage (I–V) characteristics of ClAlPc thin films, in zero grade air as the reference atmosphere, were investigated. Fig. 3 shows the I-V characteristics of ClAlPc devices in semi-logarithmic scale at different temperatures. All the results confirm that there are two distinct regions of conduction for each characteristic curve. It is also found that at low voltages below a well-defined transition voltage ($V_T$) -up to 2.5 V- devices have ohmic conduction, at higher voltages the space-charge limited conduction (SCLC) controlled by exponential trap dominates [26].

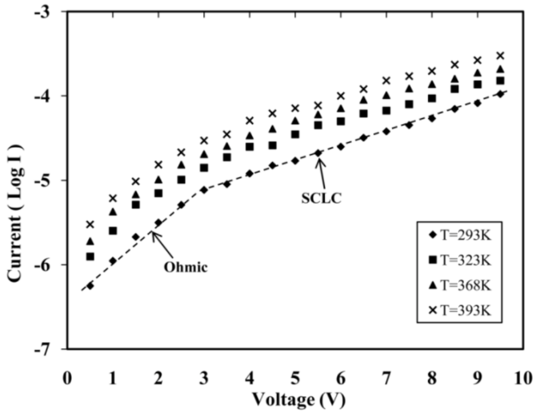

*Fig. 3. Current- voltage characteristics of devices at different temperature.*

The variation of electrical conductivity (σ) with temperature has been investigated to determine thermal activation energy and effect of chemical environments (humidity, ethanol and ammonia) on activation energy of ClAlPc thin films. An applied voltage (0.5 V) was chosen so that the devices were operating in ohmic region and measurements were carried out in the temperature range 300–420 K during cooling of devices. Linear dependence of ln (σ) on the reciprocal absolute temperature is shown in Fig. 4. The electrical conductivity of ClAlPc can be expressed as equation (1):

$$\sigma=\sigma_0 \exp(-\Delta E/2k_BT) \quad (1)$$

where σ is the electrical conductivity, ($E_{act}$ =ΔE/2) is the thermal activation energy, $k_B$ is the Boltzmann’s constant and $\sigma_0$ is the pre-exponential factor. As shown in Fig. 4, there are three distinct (linear) regions, which correspond to three activation energies $E_1$, $E_2$ and $E_3$. The three different activation energy values can be interpreted as a transition from extrinsic to intrinsic (pseudo-intrinsic) conductivity [18, 27]. The activation energy $E_1$ corresponds to non-extrinsic region, and $E_2$ and $E_3$ corresponds to extrinsic region. The activation energy corresponding to intrinsic generation is associated with resonance energy involved in a short-lived excited state, and that corresponding to impurity scattering is attributed to a short-lived charge transfer between impurity and the complex [28]. Chemical vapors can adsorb on surface of thin films and these adsorbed molecules can enhance/reduce charge carriers concentration. Analyte molecules can also act as impurity in the extrinsic conduction region [29] and change the thermal activation energy of films. At higher temperature, remained molecules can affect on conductivity of thin films in intrinsic region. The thermal activation energy of ClAlPc thin films in different chemical environments were obtained and compiled in Table 1.

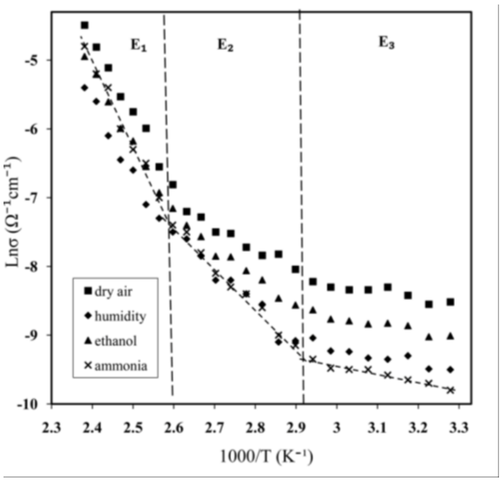

*Fig. 4. Temperature dependence of conductivity for ClAlPc devices in different chemical environments.*

*Table 1. Thermal activation energy values of ClAlPc thin films in various chemical environments.*

| Chemical environment | Activation energy (eV) | | |
|---|---|---|---|
| | $E_1$ | $E_2$ | $E_3$ |
| Dry air | 0.73 | 0.21 | 0.09 |
| Humidity (33%) | 0.67 | 0.34 | 0.05 |
| Ethanol (100 ppm) | 0.69 | 0.30 | 0.07 |
| Ammonia (100 ppm) | 0.81 | 0.36 | 0.06 |

To study the photoconductivity of ClAlPc films, they were radiated by a Quartz Tungsten Halogen (QTH) lamp

(100 W, 12 V, Newport-6333) and light intensity were measured by a digital Luxmeter (Testron, model TES-1332) in chemical environments. Devices were fixed in chamber and dark-current ($I_d$) was recorded, after that, devices were radiated and the photo-current ($I_{ph}$) was measured and current ratio ($I_d/I_{ph}$) was calculated. Fig. 5 shows the change of current ratio versus illumination (0 up to 2000 lux) for ClAlPc thin film at room temperature. All results show that the conductivity of devices increases with increase of light intensity. The charge carrier concentration may increase exponentially with the increase in the intensity of light due to band–band excitation [30]. On exposure to electron donors vapors such as ammonia and ethanol, these extra electrons and holes are immediately trapped by electron traps and acceptors and decrease the photo conductivity of thin film [29]. ClAlPc can be considered as photoconductive material and its films can be used as photodetectors.

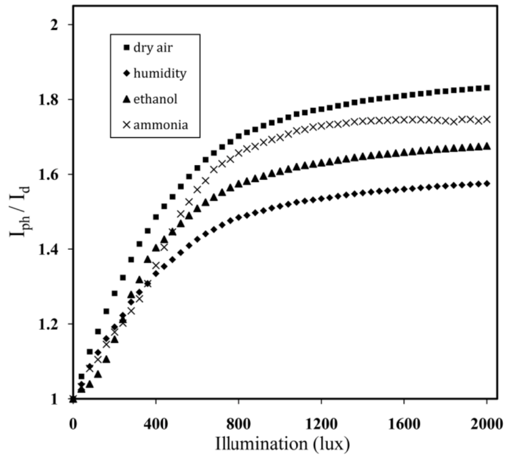

*Fig. 5. The current-illumination characteristics of ClAlPc devices in different chemical environments.*

### 3.3 Gas sensing

In the present work the gas sensitive electrical properties of ClAlPc films was investigated on exposure to humidity, ethanol and ammonia at different temperatures. The samples were fixed in a specially designed chamber and vapors were separately introduced in chamber and the sensitivity of devices versus vapors has been examined. The measurements were carried out at 25 and 100˚C for duration of 5 min. The sensitivity factor “S” is defined by the relation ($S = R_a/ R_0$) where $R_a$ is the resistance of device after exposure to analytes and $R_0$ is the initial resistance of device. As shown in fig. 6a, the sensitivity of ClAlPc films was monitored as a function of relative humidity (RH) at 25 and 100˚C. Obtained results demonstrate that the resistance of devices increases with increase of RH% and changes from 0.46 GΩ to 2.57 GΩ and from 0.20 GΩ to 1.27 GΩ at 25 and 100˚C, respectively, while RH% increases from 11% to 95%. This phenomenon is due to the adsorption of ClAlPc films, water molecules can adsorb on surface of films, and these molecules swell and penetrate inside thin films and deform them. This effect is the main cause of reduction in conductivity of films. Fig. 6b represents the sensitivity of devices versus different concentrations of ammonia and ethanol vapors at 25 and 100˚C. Ammonia and ethanol decrease the conductivity of p-type semiconductors such as Pcs. This effect is interpreted within the framework of the band theory, if we consider the adsorbed molecules to produce appropriate donor levels within the band gap of the p-type organic semiconductors, the hole concentration near the surface of films will be reduced through a doping mechanism by trapping positive holes and increase the resistance of them.

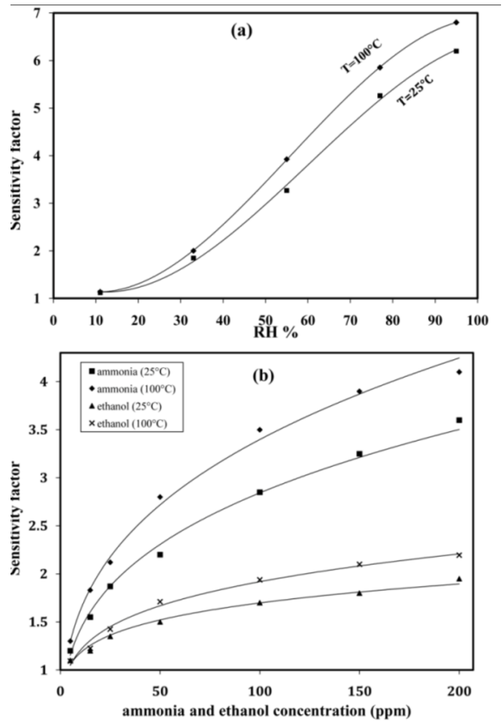

*Fig. 6. Sensitivity of ClAlPc devices versus (a) relative humidity (RH), (b) ammonia and ethanol.*

The optimal operating temperature ($T_{max}$) can be used as a parameter to calibrate gas sensors. To determine the $T_{max}$ of the sensor, the response characteristics of the devices were monitored versus 33% RH and 100ppm ammonia and ethanol at different operating temperatures in a range from 25 to 175°C. Fig. 7 shows that the operating temperature has an obvious influence on the sensitivity of devices and the sensitivity of devices increase with increase of temperature up to $T_{max}$ and decrease at higher temperatures and the $T_{max}$ was measured about 75, 90 and 105°C versus RH, ethanol and ammonia, respectively. The relationship between the gas response and the operating temperature represents a trend of ‘increase–maximum– decay’ to gases [31], temperature is able to influence on adsorption/desorption equilibrium, adsorption always refers to low temperatures ($T \leq T_{max}$) and at higher temperatures ($T > T_{max}$) the equilibrium will shift to desorption [2].

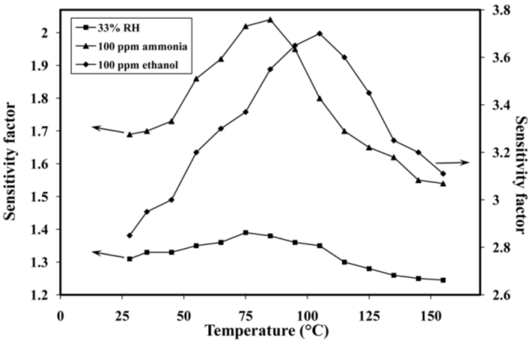

*Fig. 7. Effect of operating temperature on response of devices.*

Humidity sensors are important devices to check and calibrate working systems in different technologies. To investigate the response of devices versus humidity in chemical environments, different RH% (20- 90%) were mixed with ammonia and ethanol (1- 100 ppm) and the sensitivity of ClAlPc films was studied on exposure to humidity mixtures at room temperature. To ensure the reliability of the results, the processes repeated several times and no tangible difference has been recorded. Fig. 8 demonstrates the effect of ethanol and ammonia environments on the humidity sensing properties of ClAlPc films, humidity reduce the conductivity of devices and a similar reduction behavior was observed in ethanol and ammonia environments as a function of their concentrations. It is noticeable that the concentration of chemical vapors affects on humidity sensing and devices can be used as mixture sensors by calibrating in specific working environments.

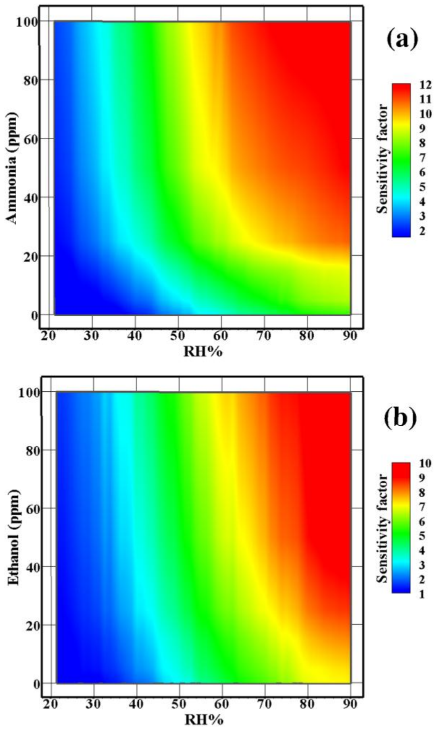

*Fig. 8. Sensitivity of ClAlPc devices versus humidity in (a) ammonia and (b) ethanol environments.*

A good humidity sensor should be focused on the improvement of the following requirements, such as linear response, high sensitivity, short response time, and long-term stability [32]. In the present study, we also tried to determine the sensing behaviors of ClAlPc thin films versus 75% RH in different chemical environments at room temperature. One of the devices stabilized in zero grade air for several hours, and then diluted vapors (humidity and its mixtures with ethanol and ammonia) were introduced into chamber and resistance change of devices was recorded. When, the resistance reached stable state, the analytes were switched off and chamber was purged, this cycle was repeated several times in chemical environments and data recorded. The dynamic response of devices is demonstrated in fig. 9, percentage of reversibility, response and recovery times of devices were calculated and indicated in Table 2. Obtained results clearly show that the resistance of devices increases after each sensing cycle and a baseline drift must take into account, the probable reason for this drift is interpreted as the effect of hysteresis (analyte molecules) on surface of thin active films after purging, analyte molecules react physically and chemically with ClAlPc. These adsorbed molecules could remove by UV, $N_2$ and heat treatments. However, some of the analyte molecules bond (covalently) with ClAlPc molecules strongly chemisorb on the surface of films.

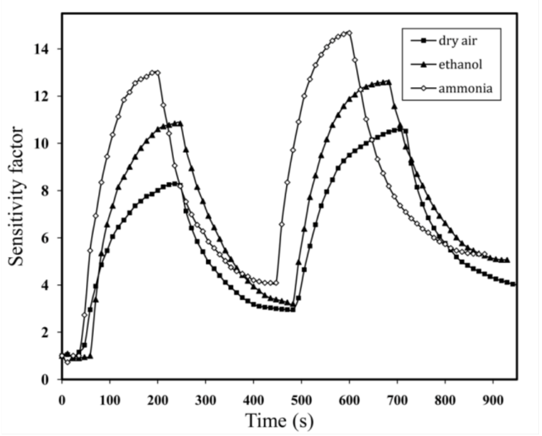

*Fig. 9. Response of ClAlPc devices on exposure to 75% RH in different chemical environments.*

*Table 2. Response of ClAlPc devices toward 75% RH in different environments.*

| Chemical environment | Response time (s) | Recovery time (s) | Percentage of reversibility |
|---|---|---|---|
| Dry air | 65 | 95 | 88% |
| Ethanol | 55 | 115 | 82% |
| Ammonia | 50 | 125 | 90% |

Finally, ClAlPc thin film devices were stored in different chemical environments for a period of 2 months and the effect of various environments on long-time stability of ClAlPc thin films was studied. Fig. 10 shows the resistance change of devices in different chemical environments, the results confirm that the resistance of devices was increased by passing time; this phenomenon was interpreted as the effect of chemical vapors and other pollutants on the conductivity of thin films. These adsorbed molecules can interact chemically with organic molecules and penetrate inside thin films. Pollutant also can deform active films and change the electrical and structural characteristics of them. The stability factor can be defined by the relation ($f_s = R_0/R_{60}$) where $R_0$ is the initial resistance and $R_{60}$ is the resistance of devices after 60 days. Obtained results also demonstrate that the stability of devices was optimum in dry air ambient ($f_s$= 94.7%), the minimum of stability was observed in ammonia environment ($f_s$ = 83.9%) and the stability factor of devices was calculated versus humidity and ethanol about 89.3 and 90.5%, respectively.

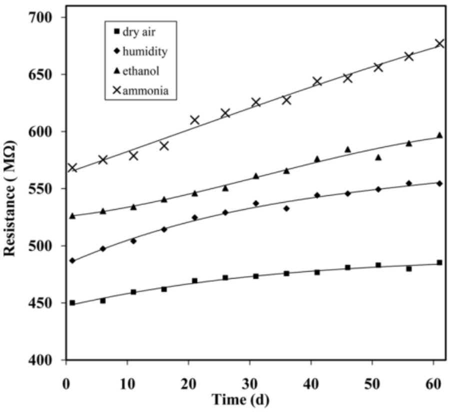

*Fig. 10. Long-time stability of thin film devices in chemical environments for 2 months.*

## 4. Conclusions

Chloroaluminum phthalocyanine (CIAlPc) nanostructured devices were prepared by thermal evaporation technique, ClAlPc thin films were deposited on interdigitated electrodes and the thickness of thin films was estimated about 200 nm. FESEM image shows that the average size of nanoparticles is about 50- 80 nm and XRD pattern confirms that ClAlPc thin films are in α-phase structure on glass substrate. Chemiresistive electrical properties of ClAlPc devices have been investigated in different chemical environments, obtained results confirm that the analytes can affect on semi-/photo-conductivity of thin films. The sensitivity of devices versus reducing vapors (humidity, ammonia and ethanol) has been investigated as function of analyte concentration and working temperature. Response analysis can be highlighted in order ammonia> humidity> ethanol and $T_{max}$ was measured about 75, 90 and 105°C versus RH, ethanol and ammonia, respectively. Devices were also used as chemiresistive sensors within the whole humidity range from 20 to 92% RH in chemical environments (1-100 ppm ammonia and ethanol) and it was found that devices can be also calibrated as humidity-selective sensor with respect to chemical vapor concentration at room temperature. The corresponding response time (50- 65 s) and recovery time (95- 125 s) of devices were measured versus 75% RH in dry air and 100 ppm ammonia/ethanol at room temperature, the percentage of reversibility of devices was also calculated in a range about 82- 90% with respect to different chemical environments. These results confirm that some analyte molecules remained on surface of thin films and decrease the sensitivity and stability of devices toward humidity. Finally, the long-time stability of devices was studied over 2 months, all results represented that the stability of devices was optimum in dry air ($f_s$= 94.7%) in comparison with other environments and the minimum of stability factor observed in ammonia environment ($f_s$ = 83.9%), this phenomenon is due to reactions between vapor and solid molecules.

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