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Surface-type multifunctional sensor based on 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin

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Abstract In this study, an organic semiconductor 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin (TIPP) was synthesized and investigated as an active material in surface-type multifunctional sensor. As electrodes, 100 nm thick Ag films were deposited on 25 mm × 25 mm glass substrate with 40 µm gap between them. Thin film of TIPP of area 15 mm × 15 mm was thermally sublimed to cover the gap between the silver electrodes. Thickness of TIPP film was 100 nm. A change in electrical resistance and capacitance of the fabricated device was observed with the increase in relative humidity (RH), temperature, and illumination. Hysteresis, response, and recovery times were investigated over a wide range of RH (0–94%). Activation energy of the TIPP was estimated. An equivalent circuit of the Ag/TIPP/Ag humidity, temperature, and illumination sensor was developed. Humidity, temperature, illumination dependent capacitive, and resistive properties of this sensor make it promising for use in a humidity, temperature, and lux multi-meters.

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Introduction

Organic semiconducting materials are being extensively studied for the fabrication of light, temperature, and humidity sensors [1–4]. There is a growing interest in the fabrication and study of surface-type devices employing organic semiconductors [1, 5–7]. Surface-type organic thin film structures represent a simple, low-cost, and versatile alternative to the devices built-in sandwich configuration for sensor applications. Surface-type organic photodetector has been studied by Agostinelli et al. [5]. The electrical properties and response time of the surface-type Ag/methyl-red/Ag humidity sensor have been investigated by Ahmad et al. [7]. This sensor showed short response time and good humidity sensitive properties. An organic semiconductor Cu(II) 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin (CuTIPP) was synthesized and investigated as an active material in photocapacitive detectors by Saleem et al. [1]. It was observed that under filament lamp illumination of up to 4000 lux the capacitance of the Al/CuTIPP/Al and Ag/CuTIPP/Ag surface-type photocapacitive detectors increased by 2.6 and 2.2 times, respectively. A sandwich-type and a surface-type photocapacitive detector employing poly-*N*-epoxypropyl carbazole complexes and copper phthalocyanine, respectively, have been investigated by Karimov et al. [6, 8]. A high-voltage photo-rechargeable photocapacitor of three-electrode configuration, comprising a dye sensitized mesoporous TiO_2 electrode, two carbon-coated electrodes and two liquid electrolytes, has been reported by Murakami et al. [9].

Sensors based on the change in electrical properties with sensing parameters are classified into two categories, namely, the resistive-type and capacitive-type. Organic thin film-based resistive and capacitive sensors have attracted a great deal of attention [7, 10–14]. Low-molecular-weight organic materials have low dielectric constant and high resistance. Both these parameters show large change with variation in environmental conditions. A thin film of polydimethylphosphazene has been used as a resistive and capacitive humidity sensor, at low or at high humidity levels [11], and a change in capacitance and resistance of about three orders of magnitude was reported with increasing relative humidity (RH) from 0 to 100%. Resistive-type humidity sensors based on polymer thin films have been reported by Sakai et al. [12].

Porphyrin-based compounds are of great interest in molecular electronics and supramolecular building blocks. Porphyrins have gained a great deal of attraction in the fabrication of electroluminescent and photovoltaic devices [15, 16] because of its natural role in photosynthesis, solution processability, and the relative ease with which functional groups can be attached to its basic structure [17]. Thin films of different metalloporphyrins have been used as sensing materials for the development of optical sensors for the detection of different volatile organic compounds [18]. In this study, we reported the synthesis of TIPP, fabrication, and the study of a surface-type multifunctional sensor employing TIPP as a humidity, temperature, and light sensitive organic semiconductor.

Experimental

Synthesis of TIPP

TIPP was synthesized by the literature methods [19, 20].

Analytical grade 4-isopropyl benzaldehyde, pyrrole, and different solvents that were employed for the synthesis of TIPP were purchased from Sigma Aldrich and used without further purification. 0.145 mol 4-isopropyl benzaldehyde (21.43 g) and 0.145 mol pyrrole (9.70 g) were added to the 500 mL refluxing propionic acid. The mixture was refluxed for 2 h and then allowed to cool at room temperature. Reaction mixture was filtered and residue was washed first in water (3 × 250 mL) and then in methanol (3 × 250 mL) to give glistering purple crystals of the title porphyrin. Recrystallization from a chloroform/methanol (2:1) mixture gave pure crystals of TIPP (6 g, 21.22%). It was characterized by UV–Vis, FTIR, elemental analysis, H NMR, and mass spectrometry. Melting points were determined on a Kofler micro-melting point apparatus without correction. IR spectra were recorded on a Nicolet Impact-410 FTIR spectrophotometer in KBr. ^{1}H NMR spectra were measured in $CDCl_3$ using TMS as internal standard with a Bruker 500 MHz spectrometer. MS spectra were taken on a KRATOS-AEI-MS50 spectrometer. Elemental analyses were performed on a PE-2400 CHN elemental analyzer. The obtained characteristics are m.p. > 300 °C (found: C, 85.71; H, 6.80; N, 7.10; $C_{56} H_{54} N_4$ requires C, 85.89; H, 6.96; N, 7.16%). ν_{max}. (KBr) 2956s, 1470m, 1348w, 1186m, 1053m, 966s, 802s, 735w, λ_{max}. ($CHCl_3$) 430, 518, 551, 593, 652 nm. H NMR (400 MHz, CH_3OD) δ 0.34, bs, 2× NH, 1.56, d, 8× (CH_3), 3.31, sep, 4× (CH), J 6.91 Hz; 8.11, d, 4× (O-Ph2H); 7.58, d, 4× (m-Ph2H), J, 7.86 Hz; 8.84, s, 4× (βCH). M/z 782.3 (M^+, 100%), 780.4 (2.14%), 391.3 (7.74%).

Device fabrication and measurements

Organic semiconductor TIPP of molecular weight 783 amu was used as an active material for sensing. Molecular structure of TIPP is shown in Fig. 1. Commercially available glass slides were used as substrates. The substrates were first cleaned ultrasonically in acetone for 30 min followed by thorough rinsing with distilled water. As electrodes, 100 nm thick Ag films were deposited on 25 mm × 25 mm glass substrate with 40 μm gap between them. Using a mask, thin film of TIPP of area 15 mm × 15 mm was thermally sublimed to cover the gap between the silver electrodes. Thickness of TIPP film was 100 nm. Thickness of the TIPP and Ag films were measured by a crystal-controlled thickness monitor. All depositions were made under the vacuum pressure of 5.5×10^{-3} Pa.

Measurements of the capacitance and resistance were done by conventional digital instruments. All capacitive measurements were made at the frequency of 1 kHz. Illumination and humidity measurements were made at room temperature. The sensor was illuminated by filament lamp. Self-made humidity chamber was used for humidity-dependent measurements in which humidity was controlled

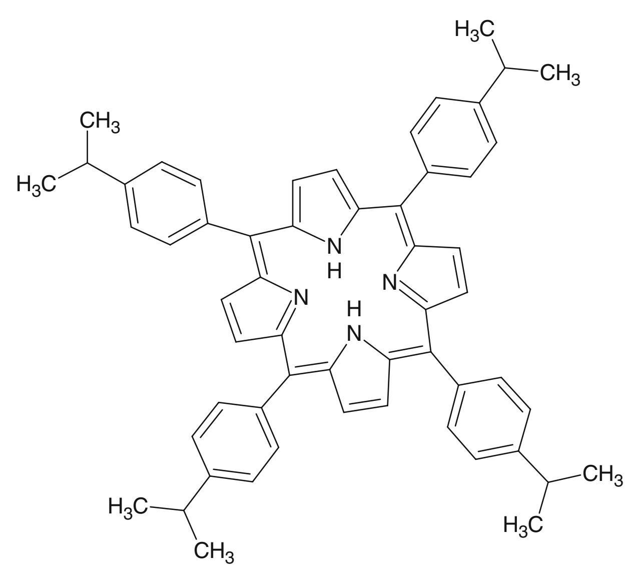

Fig. 1 Molecular structure of TIPP

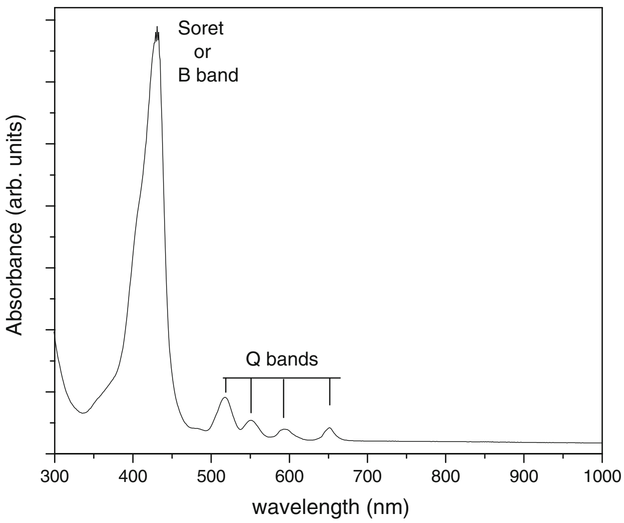

Fig. 2 Absorption spectrum of the TIPP

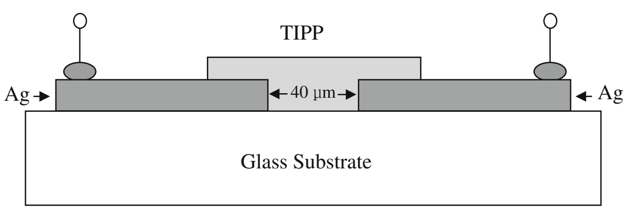

Fig. 3 Cross-sectional view of the Ag/TIPP/Ag surface-type multifunctional sensor

by a mixture of dry nitrogen and wet air. Temperature-dependent measurements were made using KARL SUSS PM5 probe station with a thermo-chuck "Alpha" series system model TP 0315A-TS-2 of Temprotic Corporation, USA.

Figure 2 shows absorption spectrum of the TIPP film deposited by vacuum evaporation on the glass substrate. The spectrum was measured using Lambda 19 PERKIN ELMER UV/VIS/NIR Spectrometer. The UV–Vis absorption bands of TIPP are due to electronic transitions from ground state (S_0) to the lowest singlet excited states S_1 and S_2 [21]. The $S_0 \rightarrow S_1$ transitions give rise to the weak Q bands in visible region at wavelengths 518, 551, 593, 652 nm, whereas $S_0 \rightarrow S_2$ transitions produces strong B band (Soret Band) in the near UV region at 430 nm. Figure 3 shows a cross-sectional view of the fabricated multifunctional capacitive–resistive sensor.

Results and discussion

The dependence of sensor resistance and capacitance at the temperature of 25 °C and zero illumination were investigated with respect to humidity variations. For humidity measurements, the sensor device was placed in a dark

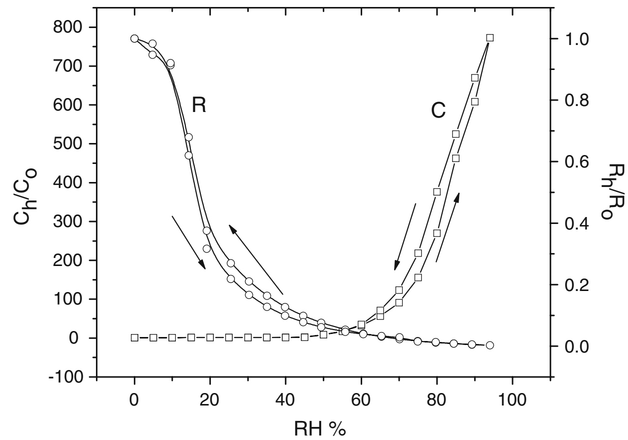

Fig. 4 Capacitance/resistance–humidity relationships for Ag/TIPP/Ag multifunctional sensor

chamber with the controlled temperature and RH. Variations of resistance and capacitance with the RH of Ag/TIPP/Ag sensor at constant temperature under dark conditions are shown in Fig. 4. It can be seen from the figure that for the variation of RH from 0 to 94%, the change in resistance is about 99 times and change in capacitance is above 773 times. At lower RH (up to 65%), sensor is sensitive for resistance, with least change in capacitance, but above that RH, capacitance increases sharply whereas resistance remains saturated in that region. A combination of these resistive and capacitive sensors can be used for larger range of RH in hygrometers. Hysteresis is a common problem in humidity sensors based on absorption and desorption. It has been determined that the sensor has an acceptable hysteresis value; capacitive measurements have a hysteresis of 7% and resistive values have a hysteresis of 6%.

Humidity sensors based on absorption and desorption typically show a nonlinear behavior as a function of RH. This behavior can be described by the following equation [22]:

$$\frac{C_s}{C_o} = \left(\frac{\varepsilon_w}{\varepsilon_d}\right)^n \tag{1}$$

where ε_d and ε_w are the permittivities of the dielectric material at dry and wet states, respectively, while the factor n is related to (the morphology of) the dielectric. The advantage of capacitive and resistive humidity measurements lies in high dielectric constant of water. Relative permittivity of water at the temperature of 20 °C is 80 [23], which is quite higher than small molecular organic semiconductors whose relative permittivity lies between 4 and 8 [24, 25]. The capacitance of a low dielectric permittivity material such as porphyrin [26] shows a huge increase upon water absorption. The same is true for resistance, where the conductance of high resistive thin films leads to an immense increase. It may be due to the displacement of currents and dissociation of water molecules into ions which cause an increase in ionic conductivity.

The response and recovery time t_{90} is an important parameter for humidity sensors. According to the literature [27], response (in case of absorption) and recovery (in case of desorption) time are defined as the time taken by a sensor to attain 90% of the total resistance/capacitance change. The response time of the sensor was measured from 47 to 94% RH at room temperature. Figure 5 shows response and recovery properties of the humidity sensor. The response time was shorter than recovery time. In case of Ag/methyl-red/Ag humidity sensor, response and recovery time were observed to be same for the capacitive measurements [8]. The response and recovery time were about 12 and 40 s, respectively, for capacitive measurements, whereas 18 and 43 s, respectively, for resistive measurements. These time durations include the equilibration time of the water vapor inside the chamber.

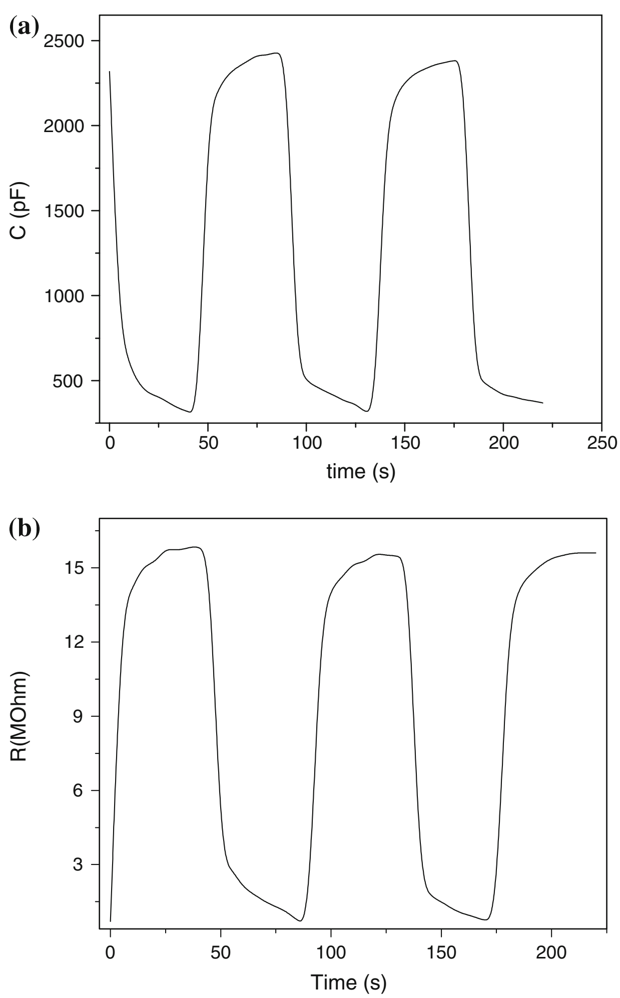

Fig. 5 Capacitance (**a**) resistance (**b**) response and recovery time to RH % variation for Ag/TIPP/Ag multifunctional sensor

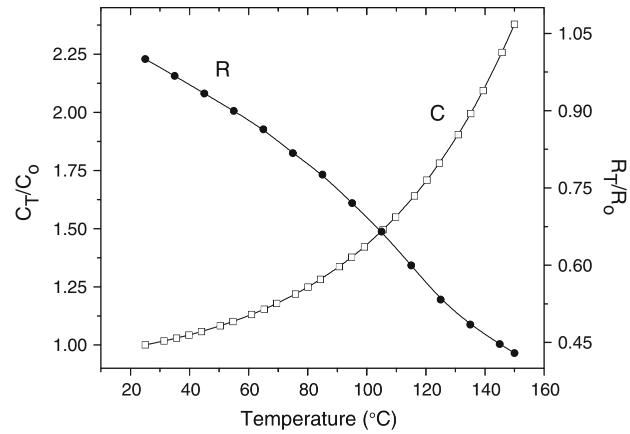

Fig. 6 Capacitance/resistance–temperature relationships for Ag/TIPP/Ag multifunctional sensor

Therefore, the real response times are much shorter. Repeated cycles between these two RH levels (47–94% RH) gave almost the same results.

Temperature versus resistance–capacitance of Ag/TIPP/Ag surface-type sensor is shown in Fig. 6. The temperature dependence of the resistance and capacitance was measured under dark conditions at 44% RH, using probe station with thermo-chuck. It has been observed that capacitance increases by 2.37 times with increase in temperature from 25 to 150 °C, whereas resistance decreases by 1.33 times for the same rise in temperature. Ag/TIPP/Ag capacitive/resistive sensor is sensitive for the whole measured temperature range (25–150 °C). Relation between resistivity and temperature is described by the following expression:

$$\rho_T = \rho_0 \exp(E/kT) \quad (2)$$

where ρ_T is the resistivity at the absolute temperature T, ρ_0 is the pre-exponential factor, E is an activation energy for conduction, and k is Boltzmann's constant. Logarithmic plot of conductivity versus reciprocal of absolute temperature is a straight line, slop of which gives the value of activation energy. Figure 7 shows a plot of ln σ (conductivity) versus 1000/T. The estimated value of activation energy from plot is 0.17 eV.

The UV–Vis absorption spectrum of TIPP (Fig. 2) indicates that absorption bands cover wide range of visible spectrum; hence, TIPP can be used as light sensor. Results of the capacitance versus illumination measurements for Ag/TIPP/Ag surface-type sensor are shown in Fig. 8. It can be seen from the figure that capacitance of the sensor increases with the increase in illumination up to 4100 lux by approximately two times, with respect to dark conditions. Ag/TIPP/Ag surface-type sensor as pohotodetector is sensitive in the range of 0 to 2500 lux for capacitive measurements. Beyond 2500 lux the device saturates and the capacitance becomes almost constant. The charge

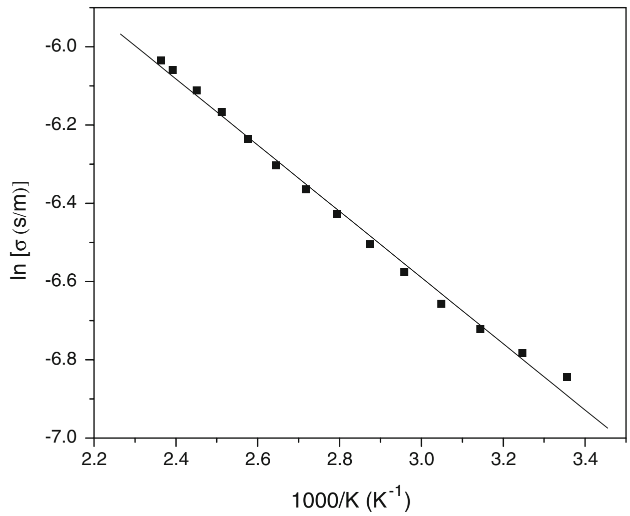

Fig. 7 Variation of ln σ (conductivity) with temperature for Ag/TIPP/Ag multifunctional sensor

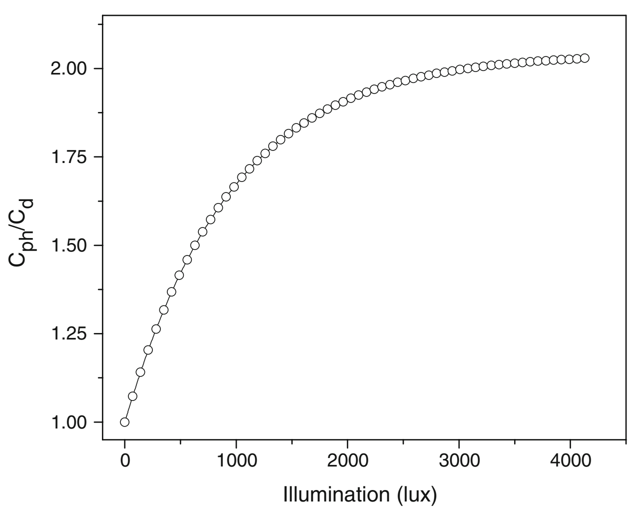

Fig. 8 Capacitance–illumination relationship for Ag/TIPP/Ag multifunctional sensor

carrier concentration may increase exponentially with the increase in the intensity of light due to band–band excitation. Therefore, the polarizability due to the transfer of charge carriers as electrons and holes may increase as well. The capacitance value depends on polarizability of the material [24, 28], and basically there are several sources of it as dipolar, ionic, and electronic polarizability. Electronic polarizability is the most universal and arises due to the relative displacement of the orbital electrons. As the TIPP may comprise internal charge-transfer complex, therefore, we may assume that ionic polarization takes place as well in this organic semiconductor. The ionic and electronic polarizability probably affects the dark capacitance at low-frequency measurements of capacitance. In earlier studies [25, 29, 30], it was investigated that polarizability, due to the transfer of charge carriers, is present both at illuminated and under dark conditions. An increase in relative permittivity of a material causes a rise in capacitance.

In Ag/TIPP/Ag sensor, the effect of light, temperature, and humidity was examined and it showed sensitivity toward these three parameters. The interaction of different effects takes place and may be minimized by fabricating the three sensors on a single substrate and casing each. In these casings, windows could be made as transparent, opaque, and porous opaque for light, temperature, and humidity sensors, respectively. Proper connections of the capacitive and resistive bridge circuitry can minimize the effect of temperature on measurement of light, or humidity. At measurements of temperature, as the sensor case is sealed, there is no effect of light and humidity. The temperature sensor will play the role of reference sensor at the measurement of light and humidity with respect to light and humidity sensors. Humidity effect is most strong with respect to the light and temperature effects. As the light and temperature sensors cased well, it may be considered that the effect of humidity is cancelled on these sensors.

A detailed equivalent circuit of the surface-type multifunctional sensor is given in Fig. 9a. C_a is capacitance with air as dielectric, and C_{ph}, C_{RH}, and C_T are capacitances with TIPP dielectrics due to illumination, humidity and temperature, respectively, whereas G_{ph}, G_{RH}, and G_T are conductances due to illumination, humidity, and temperature of TIPP, respectively. Assuming that response of the active medium of the surface-type sensor depends on humidity, temperature, and light, we developed a simplified equivalent circuit as shown in Fig. 9b as well. The equivalent circuit reflects the point that the phenomena of capacitance and resistance have a common physical reason and both are due to the generation of charge carriers (electrons/holes) under illumination, humidity, and temperature.

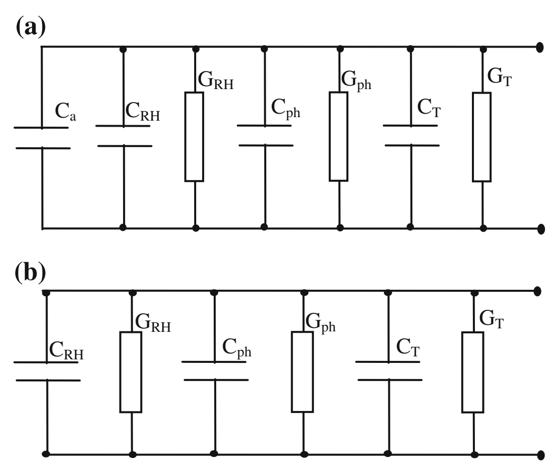

Fig. 9 Detailed (**a**) and simplified (**b**) equivalent circuit of the Ag/TIPP/Ag surface-type multifunctional sensor

Conclusions

By investigating the properties of the surface-type Ag/TIPP/Ag multifunctional sensor, it was observed that the resistance and capacitance of the sensor changes with humidity, temperature, and illumination. Change in capacitance and resistance was 773 and 99 times, respectively, for 0 to 94% RH change. It has been determined that the sensor has an acceptable hysteresis for capacitive and resistive measurements. Experimental results show that the Ag/TIPP/Ag capacitive sensor is more sensitive and quick in response than the resistive sensor. Under filament lamp illumination of up to 4100 lux the capacitance of the Ag/TIPP/Ag sensor changed by two times. Observed changes in capacitance and resistance for a change of temperature from 25 to 150 °C were 2.37 and 1.33 times, respectively. The calculated value of activation energy of TIPP was 0.17 eV. It is assumed that in general the capacitive response of the sensor is associated with polarization due to the transfer of generated electrons and holes. Resistance is also supposed to be decreased due to the generation of charge carriers under the effect of illumination, humidity, and temperature. On the basis of TIPP, multifunctional sensors potentially may be developed.

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