Humidity-dependent characteristics of DNA thin film-based Al/DNA/Al surface-type cell

Hassan Maktuff Jaber Al-Ta’ii, Vengadesh Periasamy, Yusoff Mohd. Amin

Abstract

We describe the experimental results for humidity-dependent capacitive response of semiconducting DNA thin films incorporated into Aluminum (Al)/DNA/Al surface-type Schottky diode. The DNA film was deposited using drop–casting method onto a glass substrate pre-deposited with Al followed by an Al contact to fabricate the Al/DNA/Al Schottky junctions. Alpha radiation irradiation was then carried-out for different periods (10, 20, 30 and 40 min). Results indicate an initial increase followed by a drastic drop in the resistance of the film at 257, 289, 421, 587 and 129 kΩ times and for pristine or non-radiated, 10, 20, 30 and 40 min, respectively, with a rise in the relative humidity level. It was also observed that under the effect of humidity, the capacitance of the DNA thin film increased to 935, 581, 1035, 301 and 329 nF times for the same corresponding exposure periods. The capacitive/resistive sensor was found to demonstrate a quasi-linear function with relative humidity in the range of 20–99.9% with only a small hysteresis and a response/recovery time of about 120 s. Generally, these humidity-dependent resistive and capacitive properties demonstrated in this current work may suggest utilization of Al/DNA/DNA Schottky diodes as a promising alternative for use in humidity meters.

1. Introduction

Humidity sensors are important for the determination of environmental conditions in many manufacturing applications due to the negative impacts of water vapor or humidity in an industrial environment [1]. Generally, humidity sensors can be classified by their measuring parameters, which may involve resistive, hydrometric, optical, gravimetric or capacitive either separately or integrated together [2,3]. Compared to the rest, capacitive-type humidity sensors have numerous advantages, including low power consumption and large output signals [4]. Further, the performance of such sensors is determined primarily by the properties of the hygroscopic material used in the fabrication of the sensing film and the design of the sensor electrodes [5]. In this context, organic semiconductor materials such as deoxyribonucleic acid or DNA can be utilized as the active biomaterial in the manufacture of different types of sensors for measurement of physical, chemical and biological parameters [6–9].

Many industries are especially prone to humidity fluctuations and therefore place high importance on measuring and controlling relative humidity. Therefore the pressing need for rapid and cost-effective active material to be used as the measuring element presents itself in modern industrial environments. Previous studies have demonstrated the extremely sensitive nature of semiconducting DNA molecules to variations in temperature [10,11], light [12], humidity [13], electrical field [14], magnetic field [15,16] and different types of gases [17,18]. The same sensitive response towards fluctuations in the environmental humidity levels can be expected to be exhibited by the DNA molecules since water vapor are known to significantly alter its charge transfer dynamics. Due to the obvious importance, investigative studies pertaining to organic semiconductor-based sensors such as those utilizing DNA molecules are currently an important field of research [19].

Kleine et al. investigated the humidity effect on conductivity based on the increase of ionic currents due to capillary condensation of water from immobilized DNA molecules [20]. A number of studies have also been carried-out to investigate the influence of humidity on DNA conductivity. Many of these studies on macroscopic DNA assays involve DNA networks, solid DNA, bundles of
DNA molecules and assemblies of DNA molecules [21]. Paul et al. designed DNA functionalized single walled carbon nanotube (CNT) or DFC humidity sensors based on the conductance influenced by exposure to water molecules. They observed that the sensitivity increased dramatically with the electrode gap length and bias voltage with the humidity. Optimum sensitivity was observed at a gap length of 10 μm due to higher sensing areas and does not demand drying of DNA material after the drop-casting [22]. This was similar to another work by Paul et al. who used DFC networks to fabricate Field effect transistor (FET)-based humidity sensor [23].

The experiments conducted so far could establish a clear relation between DNA conduction caused by humidity and the influence of other dimensional parameters such as DNA length or the bundle diameter [24]. However, studies pertaining to DNA behavior against alpha irradiation under varying humidity conditions have not been reported earlier. As such, this study is the first report demonstrating the effect of such parameters to DNA. In our work, we utilized a simple method to prepare the DNA thin film through the drop-casting method compared to Paul et al. [22]. Further to this, the DNA deposited between the Al electrodes follow the surface shape forming the bridge directly.

In our current study, we utilized the Al/DNA/Al surface-type Schottky diodes as the humidity sensors. Pre and post-radiation measurements under controlled chamber humidity were carried-out to quantify and establish its humidity sensing potentials. Results indicate the interesting possibility of DNA based sensors for rapid and effective detection of alpha particles.

2. Materials and methods

2.1. Preparation of the DNA solution

A simple preparation procedure of mushroom DNA extracted from colonies of fruiting bodies was used for Polymerase Chain Reaction (PCR) amplification. The procedure starts with the collection of minute quantities of mycelium (0.1–1.0 g) from a colony of the fruiting body (Stipe) of a mushroom species using a sterilized tweezer. Standard procedures according to Hibbett et al. [25] were further employed to yield pure DNA samples prior to the PCR process. The DNA of all samples was amplified by PCR (PTC-100TM, MJ Research Inc., Ramsey, MN, USA) using universal primers ITS1 forward (5′-CTC GTA GGTGA AC TC GCG-3′) and ITS4 reverse (5′-TCTCCGCTT ATT GATATGC-3′). Amplification reactions were performed in a total volume of 50.0 μl containing 10X PCR buffer 4.0 μl, dNTP mix 2.5 μl, 2.5 μl of each primer, 1.0 μl of Taq polymerase (Cosmo, Seongnam-si, Gyeonggi-do, Korea), 4.0 μl of genomic (Template DNA), and 26.0 μl of sterilized distilled water. PCR amplification was carried-out in 30 cycles at 94°C for 30 min and denatured at 50°C for 60 min, followed by annealing at 72°C for an extension of 1 min. Initial denaturing at 95°C was extended to 5 min and the final extension was at 72°C for 5 min [26,27].

2.2. Fabrication of the Al/DNA/Al Schottky diode

A glass substrate was cleaned for 15 min using deionized water (18.2 MΩ cm, Barnstead Nanopure II water system, Lake Balboa, CA, USA) in an ultrasonic cleaner and later dried in a dust-free environment. Thin films of Al (Kurt J. Lesker, Hudson Valley, PA, USA)
of 99.999% purity were deposited (thickness ∼325 nm) on the glass substrate using an Edward Auto 306 vacuum coater with a diffusion pumping system (Edward Auto 306, West Sussex, United Kingdom). While depositing the Al thin film, the pressure inside the chamber was kept at 10^{-5} mbar, whereas the deposition rate was maintained at 0.1 nm/s and the gap length and width of the gaps (between the electrodes) were maintained at 25.0 mm and 400 μm, respectively. After which, the formation of the organic DNA layer was carried-out by using a micro-syringe (Hamilton’s micro syringe, 10 μl) containing the pre-prepared DNA solution (concentration of 1.80 ng/μl). The fabricated device was then kept in a 1 K cleanroom to allow self-assembly overnight. Sample irradiation by alpha particles was achieved using a ^{241}Am source with an activity of 150 nCurie and t_{1/2} of 457 years for periods of 10, 20, 30 and 40 min. The top and cross-sectional view of the Al/DNA/Al Schottky diode fabricated is shown in Fig. 1.

The humidity meter and the Al/DNA/Al diode placed in a locked chamber were exposed to irradiation of alpha particles in a controlled humidity environment. The chamber has built-in input and output valves for gas transfer. Nitrogen gas was then passed through water and then channeled into the chamber to control and maintain a certain humidity level within the chamber. LCR meter (Instruments Instek LCR-829 LCR Meter) was used to measure the capacitance of the sensor. The in-situ capacitance and resistance values versus relative humidity (RH) measurements of the Al/DNA/Al sensor at ambient temperature (25 ± 1°C), were carried-out by placing the device in the hermetically sealed humidity chamber capable of providing a humidity range of 20–99.9% RH. Fig. 2 illustrates the experimental setup used for the measurements.

**Fig. 3.** Graphs (a) capacitance versus relative humidity, (b) hysteresis curve for the Al/DNA/Al humidity sensor while the arrows refer to either increase in the RH% (↑) or reduction in the RH% (↓).

**Fig. 4.** Relation between the resistance and capacitance with humidity for Al/DNA/Al junctions.
3. Results and discussion

Fig. 3(a) shows the relationship between capacitance and RH within the range from 20 to 99.9%. Measurements were taken for the Al/DNA/Al humidity sensor for non-radiated and radiated (for 10, 20, 30 and 40 min) samples at 0.8 kHz and 1 V. From the experimental results, the capacitance was observed to increase with higher humidity, which demonstrates sensitivity to humidity in the studied range. Higher water molecule content at high humidity levels increases the dielectric permittivity constant, thereby acting to improve the capacitance of the device [24,28]. This in turn increases conductivity as a result of the rise in electron transport along the dsDNA helix [29].

In the case of decreasing humidity, a deviation was observed instead. Table 1 shows the capacitance values in three distinct ranges. In the range 99.9%, the highest capacitance values were 55,102, 31,617 and 28,071 nF for non-radiated, 40 and 20 min samples, respectively. For RH of 45%, 40 min registers the highest value (0.90475 nF) followed by non-radiated (0.20463 nF) and 20 min of radiation (0.15522 nF). This trend changed again at the RH value of 20%, where 40 min is the highest followed by non-radiated and 30 min (0.09613, 0.05894 and 0.03142 nF, respectively). In the last two cases, the 30 min samples registered the lowest capacitance values contrary to the highest RH environment. This deviation occurred during the decline in the RH level, whereas the capacitance of the device reduced due to desorption of water molecules. The results presented in Fig. 3(b) demonstrate that during the reversal, the capacitance does not follow the same behavior causing the hysteresis cycle. The hysteresis is common in adsorption based humidity sensors. Some factors contributing to this effect are porous structure and surface morphology of the sensing layer [30]. As a result of this deviation, the hypersensitivity phenomena can be indicated. The occurrence of the hypersensitivity phenomena results in the DNA gaining some resistance or self-protection after irradiation. The effect involves additional breaks in the sugar-phosphate molecular chains. These breaks might also result in further separation to occur in the DNA chains, threatening the life of the cell.

Hysteresis occurs as a result of the ratio between the response observed during increasing and decreasing (reversal) RH values. This factor is considered significant to establish the absorption principle for the humidity sensor. The formation of clusters of absorbed water, pores size, film thickness and the deviation in pores geometry with RH leads to the hysteresis. Sensitivity and response time were found to decline due to the large pore size [31,32]. The results presented in Fig. 3(b) shows that reversal RH profile for capacitance does not match the increasing RH profile driving the formation of the hysteresis loop. The hysteresis fluctuates with increasing irradiation time with values of 4.665, 4.1475, 9.4362, 7.3834 and 4.2893 for non-radiated, 10, 20, 30 and 40 min samples, respectively. A sharp increase was observed for the 30 min sample. The high hysteresis may be due to the fact that the film is thick and has a rough surface caused by the irradiation impact.

Capacitance and the resistance were observed to increase with decreasing humidity. The capacitance increases exponentially together with the humidity, which follows a S-shape as shown in Fig. 4(b). This could be due to the decrease in resistance in response to the increase in H2O molecule concentration and displacement currents, and the concentration of charge carriers doped by water molecules [33]. Leveritt et al. found that increasing the humidity results in the corresponding dramatic increase in the DNA conductance where the electrical field confinement inside water molecules induced the ion binding energy [34]. Ajore et al. [35] observed that the humidity also lead to structural distortion phenomena, which is considered a significant parameter responsible for DNA nanowire
conductivity properties. They reported quantitative changes in the conductivity values corresponding to the humidity conditions. The humidity impact on the resistance and capacitance of the samples can be attributed physically to the absorption and adsorption of water molecules, and therefore the organic material permittivity leading to the increase of capacitance. Furthermore, the resistance decreases due to the displacement of current, which is linked to the motion-bound charges of the water molecules [36].

As shown in Fig. 4(a), the resistance declines exponentially with increasing relative humidity. Specifically, it decreases rapidly by about four orders of magnitude at a relative humidity of 60–99.9%. Overall, the resistance drops dramatically from (1678, 2949, 2813, 9999 and 692.5) kΩ at 20% RH to (6.526, 10.21, 6.684, 17.03 kΩ at 99.9% RH.

Fig. 6. AFM images of (a) non-radiated and (b, c) radiated Al/DNA/Al sensors.
and 5.383 kΩ at 99.9% RH for the non-radiated, 10, 20, 30, and 40 min, respectively. The resistance decreased exponentially and was attributed to adsorption of water molecules by the DNA. This change is explained as follows; DNA consists of three portions, which are the bases, sugars and phosphate groups. The hydrophilic phosphate group around the base pairs of DNA causes the water molecules to be easily absorbed by forming hydrogen bonds between them.

The sensitivity versus RH% curve for all the fabricated devices plotted in Fig. 5(a) agrees well with results reported by Paul et al. [22]. As the sensitivity rises exponentially with RH%, it was observed that the device was more sensitive at higher RH% compared to lower RH% values. This could probably be attributed to the increase in the DNA conductance with increasing humidity and the ionic conduction [22], which lead to change in the electronic relocalization in the nucleobases [37]. The protons tunnel or transfer from one water molecule to the other and was able to create hydrogen bondings with the water molecules [2]. The humidity sensing ability of this type of capacitive device rely on elements such as the area of the electrodes and the distance between the electrodes [38]. The Al/DNA/Al device can be considered as a surface plate capacitor, assuming that the face edges of the electrodes act as parallel layers. As such, the capacitance of the sensor can be measured using the following method [39–41]:

\[ C_{eq} = C_0 = \varepsilon_{0}A/d \]  

where \( C_0 \) is the initial capacitance, \( \varepsilon \) represents the relative dielectric constant, \( \varepsilon_{0} \) the absolute permittivity, A is equal to the area of the surface and \( d \) the distance between the electrodes. Eq. (2) has meanwhile, expressed the capacitance affected by the humidity effect. This equation can also be obtained by fitting the sensor under higher humidity levels

\[ C = \varepsilon_{eq}A(1 + m_1 H)/d(1 - m_2 H) \]  

where \( H \) is the RH level and \( m_1 \) and \( m_2 \) are the constants. In the case of relative capacitance, Eq. (2) can be rewritten as;

\[ C/C_0 = (1 + m_1 H)/(1 - m_2 H) \]

From Eq. (3), the following simple equation can be derived;

\[ C/C_0 = aH + b \]  

Fig. 5(b) shows the experimental and simulated results where the latter were calculated using Eq. (4). Table 2 lists the sensitivity and value (a) of the slope in Fig. 5(b) and value (b) from Eq. (4) for both the non-radiated and radiated structures (10, 20, 30 and 40 min).

3.1. Atomic force microscope and field effect scanning electron microscope (FESEM)

Atomic Force Microscope (AFM) (Q-Scope Series, Ambios Technology, Germany) image was examined to study the surface.
Table 2
Sensitivity values and other parameters measured from the Al/DNA/Al Schottky barrier diode-type humidity sensor.

<table>
<thead>
<tr>
<th></th>
<th>Non-radiated</th>
<th>10 min</th>
<th>20 min</th>
<th>30 min</th>
<th>40 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope (a) (arb.)</td>
<td>0.042</td>
<td>0.0401</td>
<td>0.0414</td>
<td>0.034</td>
<td>0.03217</td>
</tr>
<tr>
<td>b (1/%RH)</td>
<td>-1.156</td>
<td>-1.023</td>
<td>-0.961</td>
<td>-1.068</td>
<td>-0.5116</td>
</tr>
<tr>
<td>Adj. R-Square</td>
<td>0.98297</td>
<td>0.98084</td>
<td>0.98095</td>
<td>0.95635</td>
<td>0.98932</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>0.6889</td>
<td>0.20437</td>
<td>0.35099</td>
<td>0.11808</td>
<td>0.3945</td>
</tr>
</tbody>
</table>

![Graph 1](image1.png)  
**Fig. 8.** Response-recovery graph for the Al/DNA/Al humidity sensor.

The absorption and numerous tracks resulting from the alpha particle irradiation lead to the “spongy” looking film surface, which consists mostly of water molecules. The electrical response also increases with the humidity due to efficient distribution of the water molecules. To evaluate the performance of the Al/DNA/Al sensor, its response and recovery behaviors can be examined experimentally, which are considered some of the most significant features for evaluating any type of sensors [39,42,43]. The surface morphology of the DNA films was also investigated using Field Effect Scanning Electron Microscope (FESEM) as shown by the images in Fig. 7. The porous nature of the film’s surface can be clearly seen in the surface morphology images. This porosity endorses the diffusion of water molecules, which enhances the electrical response to humidity.

3.2. Response and recovery time

The profiles in Fig. 8 demonstrate the capacitive response of the Al/DNA/Al structure exposed to a fast variation of humidity (5–95% RH). The electrical response of the sensor becomes unstable when exposed to a RH value of 95%, followed by a rapid and sharp change back to its unique values within 5 s upon replacing the tested vapor condition. Response and recovery time characteristics of the Al/DNA/Al sensor were measured at a frequency of 800 Hz under a RH condition of 5%.

Fig. 8 also demonstrates the sensors’ response time (humidification from 5% to 95% RH), which was at 88.701, 94.831, 105.168, 95.913 and 96.995 s for the non-radiated, 10, 20, 30 and 40 min, respectively. The relative capacitance of the sensor increased from 4.0 (5% RH) to 1035 nF (95% RH). When exposed to the maximum humidity of 95% RH, values observed were 175, 780, 1035, 550 and 650 nF for the non-radiated, 10, 20, 30 and 40 min, respectively, while the recovery time (drying effect, 95–5% RH) was 107.331, 113.461, 125.8413, 108.293 and 118.5096 s for the non-radiated, 10, 20, 30 and 40 min, respectively. Both types of responses (humidification and drying) illustrate obvious changes due to some hysteresis effect [44]. These changes are highly dependent on the thickness of the structure [45] and may also be attributed to permanent structural defect due to the alpha irradiation. Fig. 9 demonstrates the relation between the sensitivity of the Al/DNA/Al sensor with the irradiation time. From this figure, the sensitivity was observed to fluctuate with irradiation period, which can be attributed to the hypersensitivity phenomena of the DNA and the increasing number of alpha particle tracks.

4. Conclusions

In this study, DNA thin film deposited by the drop-casting method was utilized as a humidity sensor in the form of Al/DNA/Al structures. The sensors fabricated were studied in the humidity range of 20–99.9% RH and demonstrated good sensitivity between 90 and 99.9% RH. Results also showed that with the rise in humidity, capacitance rises, whereas the device resistance dropped. Resistance and capacitance-humidity relationships recorded significant variations in the range of 45–75 and 60–99.9% RH. The resistance of the film generally reduced from a high of 1678 to a low of 6.523 kΩ and 9999–17.03 kΩ for the non-radiated and 30 min of alpha irradiation, respectively. It was also shown that under the effect of increasing humidity, the resistance of the film reduced to 257, 289, 421, 587 and 129 kΩ times for non-radiated, 10, 20, 30 and 40 min, respectively with a rise of the RH level over the whole humidity range. It was also observed that under the effect of humidity from the highest to the lowest, the capacitance of the DNA thin film increased by 935, 581, 1035, 301 and 329 times for non-radiated, 10, 20, 30 and 40 min, respectively. The capacitance of DNA thin film increased between 0.02712 to 55.102 nF for both the non-radiated and irradiated samples. These observations show the exciting possibility of utilizing Al/DNA/Al Schottky barriers as potentially sensitive humidity sensors for detecting alpha radiation.

**Author contributions**

H.M.J.A.-T and V.P. conceived and designed the experiments; H.M.J.A.-T performed the experiments; H.M.J.A.-T and V.P. analyzed the data; V.P. and Y.M.A. contributed reagents/materials/analysis...
Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

Financial assistance provided by the Fundamental Research Grant Scheme, FRGS (FP004-2013A), University of Malaya Research Grant, UMRG (RG321-15AFR) and University of Malaya Post-graduate Research Fund. PPP (PG202-2014B) grants are greatly appreciated. We would also like to thank Dr. Khaleda Sulaiman and Dr. Zubair Ahmad for their valuable advices on instrument diagnostics and analysis. The first author would like to thank the Ministry of Higher Education and Scientific Research of Iraq for the financial assistance provided for his PhD study.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2016.03.093.

References