

Humidity effect on electrical properties of graphene oxide back-to-back Schottky diode

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Abstract

A Schottky diode-based sensor is a promising structure for high sensitive and low power sensor. This paper investigates a device called back-to-back Schottky diode (BBSD) for humidity sensing operation. The BBSD provides simpler device configuration that can be fabricated using less complicated process. The current-voltage characteristic of the fabricated BBSD was measured at different relative humidity. From the obtained characteristics, series resistance, barrier height and ideality factor was analyzed. The device current increased at higher humidity level. The current increase could be associated to the decrease in series resistance, barrier height and ideality factor. When humidity decreased from 11% to 97%, the barrier height showed reduction of 0.1 eV. The barrier height reduction was explained by considering electric field-induced reduction of graphene oxide. The observed result confirmed the device feasibility as promising simple and low cost humidity sensor.

Keywords: back-to-back Schottky, graphene oxide, humidity sensor

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1. Introduction

Graphene oxide (GO) is a graphene derivative which has been attracting a lot of attention because of its potential for mass production at considerable cost. GO is regarded to be favorable for applications such as transparent electrode, conductive ink, chemical sensor, photodetector and so on [1-6]. Owing to the presence of defective sites across the planes and the edges, the GO flake can be chemically functionalized in order to modify and enhance its electrical properties [7, 8]. As for sensor application, GO has been intensively studied for many targeted analytes using various device structure such as resistive-, transistor- and diode-based structure [3-5].

A Schottky diode-based sensor is considered to operate with better sensitivity and lower power consumption compared with the simple resistive-based sensor [9]. Multiple reports have demonstrated and evaluated the sensing operation of graphene Schottky diode [9-11]. In our previous works, fabrication and analysis of a device called back-to-back Schottky diode (BBSD) was presented [12, 13]. The highlighted advantage of the BBSD over the normal Schottky diode is its simple structure that required less fabrication step. Technique to analyze the Schottky junction properties in the device was also described in our previous work [13]. In comparison to normal Schottky diode, reported work on sensing operation of BBSD device is relatively limited.

This paper presents the functionality study of GO-based BBSD structure as humidity sensor. Schottky junctions are formed between GO and n-type silicon (n-Si) substrate. In order to analyze its sensing operation, the current-voltage (I-V) characteristics of the device were measured at different relative humidity (RH). In case of Schottky-based sensor, the sensing operation is generally related to the modification of barrier height at the Schottky junction. The Schottky junction properties, namely barrier height and ideality factor, were extracted and its dependence to the humidity level was discussed. Understanding the mechanism is significant as it hold key information in designing more optimized sensor structure.

2. Research Method

Figure 1 shows the fabrication flow of a simple GO-based BBSD. The device structure consists of two GO electrodes on n-Si substrate (resistivity: 1-10 Ω cm). These electrodes are expected to form Schottky contact on the n-Si surface. The first stage of device fabrication was formation of GO thin film via spin coating of concentrated GO aqueous dispersion. The concentrated GO aqueous dispersion was prepared by heating 30 ml GO dispersion (4 mg/ml, Graphenea Inc, USA) at around 100 °C. The heating was stopped after the volume of the dispersion reduced to 20 ml. Prior to the spin coating, Si substrate was cleaned using diluted hydrofluoric acid (HF) for native oxide removal. The GO dispersion was spin coated onto Si substrate using spin coater at 4000 rpm for 30 seconds. The film was left to dry at room temperature.

Then, the two GO electrodes were defined by delaminating middle part of the GO thin film using adhesive tape. As labelled in the figure, the two electrodes are denoted as SE1 and SE2. The area of SE1 and SE2 are 0.43 and 0.34 cm^2 , respectively. It was difficult to control the exact area of two GO electrodes as a very simple delaminating procedure was employed. Nevertheless, the contact area is not critical from the point view of this work. Finally, the fabricated device was mounted on glass slide and electrical connections were formed to enable voltage application and current flow through the GO electrode. Figure 2 shows how the electrical connection was made using silver paste, copper thread and copper tape.

In order to investigate the influence of different ambient humidity, the sample was characterized inside a sealed glass bottle. Figure 3 shows the measurement setup. In order to produce certain RH level, a specific type of saturated salt solution was put inside the bottle [14, 15]. Table 1 states the used salt solution and its resulting RH ambient. Several drops of deionized water were added to few tablespoons of the salt until it became slurry. The salt slurry and the device were placed inside the sealed bottle. After several hours, the RH level is fixed at certain level. The RH level monitoring was done using another RH meter. Then, the device current-voltage (I-V) characteristic was measured using Agilent B1500a Parameter analyzer. After the measurement, the saturated salt was replaced and the measurement was repeated. The setup and procedure used in this work has been employed in many works to characterize and calibrate humidity sensor [16].

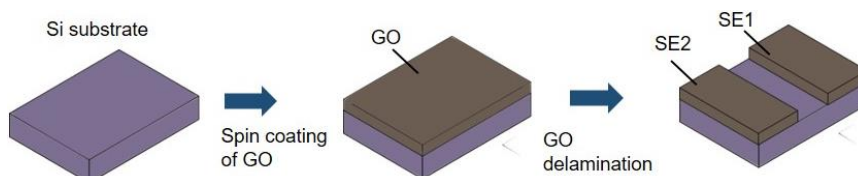


Figure 1. Process flow of device fabrication

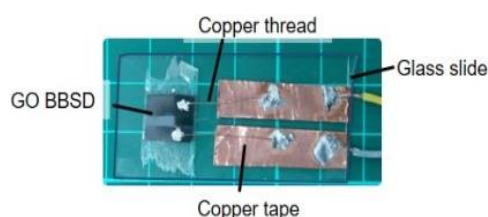


Figure 2. Actual fabricated device

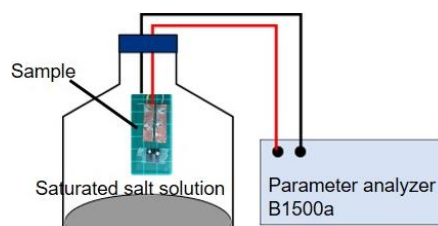


Figure 3. Measurement setup

Table 1. The salt and the generated relative humidity [14]

Salt	RH (%)
Lithium chloride	11.3
Magnesium chloride	32.8
Magnesium nitride	52.9
Potassium chloride	84.3
Potassium nitride	93.6
Potassium sulfate	97.3

3. Results and Analysis

3.1. I-V Characteristics at Different RH

Figure 4 shows I-V characteristics of the fabricated device at RH range from 11.3% to 97.3%. The observed characteristics resemble a typical I-V curve for the BBSD structure reported at other work [17, 18]. According to the metal/semiconductor contact theory, a potential barrier is expected to form at GO/Si interface due to work function difference [19]. The potential barrier restricts the flow of current at low applied voltage. As the voltage increases, the potential barrier height decreases due to the so-called image force barrier lowering effect. The effect leads to more current flow at higher voltage. In contrast with normal Schottky diode, the BBSD device has poor rectification behavior. The rectification ratio was calculated to be less than one.

Device under high RH ambient generally produced higher current. The trend could be clearly observed particularly at high positive voltage. The highest current was obtained under RH of 97.3%, while the lowest current was when RH is 11.3%. Static resistance (R_D) at 10 V was calculated and plotted as a function of RH in Figure 5. The resistance decreased as the RH increased. Although the result showed poor linearity, it indicates the possibility of using the BBSD device as humidity sensor. For RH range below 52.9 %, the sensitivity was estimated as 15.7 k Ω /%. For RH above the 84.3 %, the sensitivity was 6.9 k Ω /%. Further investigation is required to evaluate the sensor performance such as linearity and sensitivity.

On the other hand, the progressive trend could not be observed at negative voltage. Based on the ideal operation of the BBSD structure, the I-V for positive and negative voltage regime should be symmetrical as the two Schottky electrodes are made from same material (i.e. GO) and has almost identical contact area. The positive bias operation depends on the SE2 Schottky junction. The negative bias operation depends on the SE1 Schottky junction. In order to understand the reason for the current changes, the change of junction properties towards different RH for the two Schottky electrodes is analyzed in the next section. The discussed junction properties are series resistance, barrier height and ideality factor.

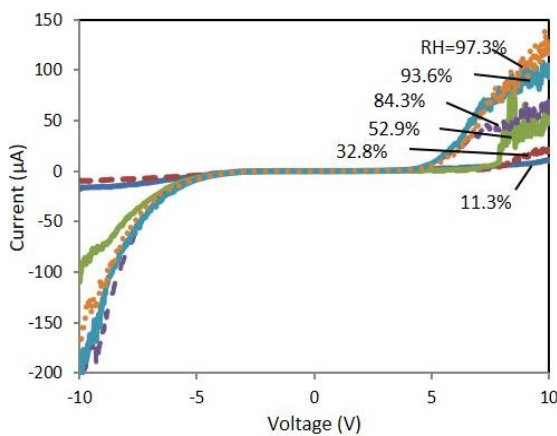


Figure 4. I-V characteristics at different RH

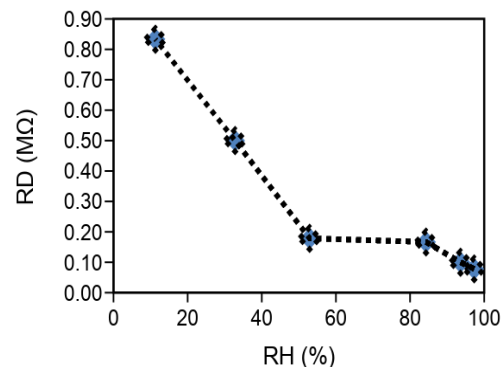


Figure 5. Static resistance calculated at 10 V as a function of RH

3.2. Series Resistance, Schottky Barrier Height and Ideality Factor Analysis

The BBSD structure can be modelled using equivalent circuit shown in Figure 6 [13, 17, 18, 20]. SE1 and SE2 are represented by two schottky diodes connected in back-to-back manner. The current transport of the diode is assumed to follow thermionic emission theory. Along the electrical conduction path in the structure, voltage drop occurs due to resistance from Si substrate, GO and connection. The sum of these resistances is considered as series resistance (R_S). When voltage is applied, either one of the diodes is in reverse-biased condition. This diode will control the overall current flow in the BBSD structure. At positive V_A , current is determined by SE2. On the other hand, current at negative V_A is determined by SE1. Current equation of the BBSD can be expressed using (1) [13]:

$$I \approx \begin{cases} I_{S2} \exp\left(-\frac{q(V_A - IR_S)}{n_2 kT}\right) \left[\exp\left(\frac{q(V_A - IR_S)}{kT}\right) - 1 \right] & \text{if } V_A > 0 \\ I_{S1} \exp\left(\frac{q(V_A - IR_S)}{n_1 kT}\right) \left[1 - \exp\left(-\frac{q(V_A - IR_S)}{kT}\right) \right] & \text{if } V_A < 0 \end{cases} \quad (1)$$

I_{S1} and I_{S2} are saturation current for SE1 and SE2, respectively. T is the temperature in Kelvin, q is the elementary charge and k is the Boltzmann constant. n_1 and n_2 are ideality factor for SE1 and SE2, respectively. The factor indicates how well the experimental I-V curve can be fitted by the thermionic theory. Saturation current of the Schottky junction is defined by (2) and (3).

$$I_{S1} = S_1 A^* T^2 \exp\left(-\frac{q\phi_{B1}}{kT}\right) \quad (2)$$

$$I_{S2} = S_2 A^* T^2 \exp\left(-\frac{q\phi_{B2}}{kT}\right) \quad (3)$$

S is contact area, A^* is Richardson constant and $q\phi_B$ is Schottky barrier height. Richardson constant for n-type silicon is $112 \text{ Acm}^{-2}\text{K}^{-2}$. By using the above equations and technique described in our previous paper, series resistance, barrier height and ideality factor could be extracted [13, 21].

At high bias region of the I-V curve, the current is limited by the value of R_S . Thus, R_S can be estimated from the slope of the I-V curve at high bias region. Figure 7 shows the extracted value as a function of RH. When humidity increased from 11.3 to 52.9%, the R_S markedly decreased. R_S is the total resistance from GO electrode, substrate and interconnection. The reduction in R_S value might be due to decrease of GO film resistance. At high humidity, water vapors are absorbed on the surface of GO electrode. Interaction between water molecules and functional chemical group attached to the GO produced conductive H^+ [22]. The ion conduction improves the conductivity and hence reduces the resistance. Above the 52.9%, no significant change and clear trend could be observed. Current fluctuation especially in I-V curve for RH=52.9% might have affect the estimated value. We speculate that beyond the 52.9% RH, the value of R_S is no longer determined by the resistance of GO electrode. Other factors such as substrate and interconnection resistances might have limited the R_S value. In case when the humidity effect needs to be suppressed, the GO electrode should be chemically reduced. The reduced GO will have lower resistance and lesser interaction with humidity [23].

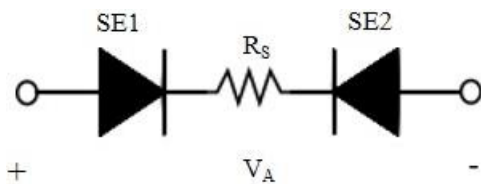


Figure 6. Equivalent circuit of the BBSD structure

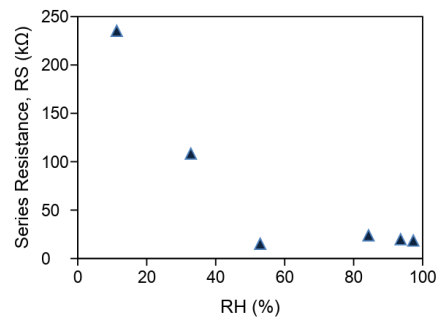


Figure 7. Series resistance as a function of RH

The extracted barrier height and ideality factor for SE1 and SE2 are shown in Table 2 and plotted as a function of RH in Figure 8. The barrier height of both Schottky electrodes was found to decrease when humidity is higher. This indicates the possible interaction between GO film and water vapor at different humidity. According to the Schottky-Mott rule, the barrier height of a Schottky junction is equal to the difference between GO work function (ϕ_{GO}) and Si electron affinity (χ_{Si}) [19].

$$q\phi_B = \phi_{GO} - \chi_{Si} \quad (4)$$

Since the electron affinity is a fixed value, the change of barrier height could be associated to the modification of GO work function. The GO work function is known to be highly dependent to the absorbed molecules and attached functional groups [24]. Based on the obtained result, it can be said that GO work function decreases as humidity becomes higher. As for ideality factor, the value became closer to unity when RH increased. Several factors that contribute to the non-ideal curve are defects at the interface, image force barrier lowering effect and modulation of GO work function by electric field [25]. At high RH, these factors are speculated to become less dominant. Thus, ideality factor close to unity was achieved.

Table 2. Barrier Height and Ideality Factor of SE1 and SE2 at Different RH

RH (%)	Barrier height (eV)		Ideality factor	
	SE1	SE2	SE1	SE2
11.3	0.98	0.92	1.086	1.054
32.8	0.99	0.90	1.075	1.038
52.9	0.94	0.90	1.065	1.041
84.3	0.91	0.84	1.053	1.022
93.6	0.90	0.81	1.048	1.014
97.3	0.94	0.82	1.063	1.017

Based on the results from junction properties analysis, it can be concluded that the change of R_D in Figure 4 is as a result of change in R_S and barrier height. For operation at RH below 52.9%, R_S seems to be the dominant factor that affects the BBSD resistance. On the other hand, for operation at RH above 84.3%, the R_D change might be contributed by the variation of Schottky barrier height.

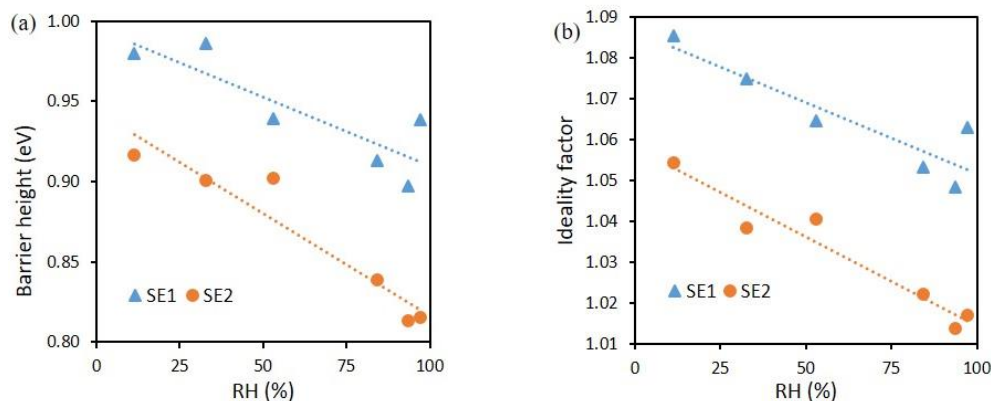


Figure 8. (a) Barrier height and (b) ideality factor at different RH value for SE1 and SE2

3.3. Mechanism for Schottky Barrier Height Reduction

As explained in the previous section, the obtained result indicated the decrease of GO work function at higher humidity ambient. However, this is in contrast with the widely accepted fact that water vapor is considered as an electron withdrawing molecule (EWM) for graphene [10]. In general, the EWM produces hole by withdrawing electron from graphene. Such p-type doping process should lead to the increase in work function and subsequently results in higher barrier height. The above mechanism could not explain the result in this paper.

The result in this paper was found to be quite similar to observation by A. Singh et al. [9]. In their work, the n-type Si Schottky diode produced higher current after exposure to more EWM. Nevertheless, no detailed explanation was provided. One possible mechanism that can explain our result is based on electric field-induced GO reduction [22]. At high voltage and high humidity, interlayer water molecules are ionized and produce hydrogen ion and hydroxyl ions. Then, GO is reduced to become reduced graphene oxide (rGO).



Conversion to rGO leads to reduce of work function due to the reduction of oxygen content. According to (5), the decrease of work function makes the barrier becomes lower. In order to validate the described mechanism, further investigation is required.

4. Conclusion

A simple GO/Si BBSD structure was fabricated to investigate the feasibility of using it as humidity sensor. The current magnitude of the device was shown to increase at higher humidity level, thus confirming the ability to sense water molecules. Further analysis is required for thorough analysis of the sensor performance. Then, the sensing operation was analyzed by extracting series resistance, barrier height and ideality factor. Possible explanation regarding the changes of these parameters was discussed. Finally, a mechanism describing how the barrier height is reduced under high humidity was presented. Electric field-induced GO reduction is speculated to be the key process. Although more thorough analysis is required to evaluate the sensing performance and to understand the device sensing operation, this experimental result opens up possibility of realizing simple humidity sensor using GO.

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