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Short communication

Influence of the oxygen content on the humidity sensing properties of functionalized graphene films based on bulk acoustic wave humidity sensors

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ABSTRACT

In this work, functionalized graphene films with different oxygen contents were prepared and their humidity sensing properties, such as humidity response, humidity hysteresis, dynamic response and recovery, were studied by combining them with a bulk acoustic wave sensor. The experimental results revealed that the humidity sensing properties of the functionalized graphene films were strongly associated with their oxygen content. The humidity response of the sensor could be improved by increasing the oxygen content of the functionalized graphene films. The stability of the sensor was also investigated using an impedance analysis method. The results indicated that the stability of the sensor was also influenced by the oxygen content of the functionalized graphene films during humidity detection. An increase in the oxygen content of the functionalized graphene film reduced the sensor stability. Thus, our work suggests that the oxygen content of functionalized graphene films is a key parameter for the design of graphene-based bulk acoustic wave humidity sensors.

1. Introduction

Relative humidity (RH) plays a significant role in many fields, such as meteorology, agriculture, manufacturing, food storage and so on [1,2], as it is an important environment parameter. The constantly increasing demand for humidity sensors in the market has stimulated much research on the development of high performance humidity sensors. In the past half century, acoustic wave transducers, including bulk acoustic wave (BAW) [3] and surface acoustic wave (SAW) [4] transducers have received a large amount of attention in the gas and humidity sensor fields. Particularly, quartz resonators, also frequently referred to as quartz crystal microbalances (QCMs) in the sensor field, are important BAW devices that are widely used for gas or humidity detection by combining them with a target adsorbed layer. QCM transducers are simple to manufacture, are able to withstand harsh environments, are thermally stable, and have a high mass sensitivity. The detection principle of a QCM sensor is based on the Sauerbrey relationship, as shown in Eq. (1) [5]. In this equation, f_0 is the fundamental resonance frequency of the QCM; Δm is the additional mass on the electrode; ρ_q and μ_q are the density and shear modulus of quartz, respectively; and A is the surface area of the electrode. It should be noted that this relationship is only valid for the characterization of rigid films. However, the hygroscopic materials that are used in QCM humidity sensors do not all have the same rigidity. As a result, Dong derived a frequency shift expression to describe non-rigid, hygroscopic material-based QCM sensors, as shown in equation [6]. Here, ρ_L and η_L are the density and viscosity of hygroscopic material, respectively. It can be found that the increase in the viscosity of the hygroscopic material increases the frequency shift. However, in addition to the frequency shift, an increase in the viscosity of the hygroscopic material due to water adsorption will reduce the quality factor (Q) and the stability.

$$\Delta f_{\text{rigid}} = -\frac{2f_0\Delta m}{A\sqrt{\rho_q\mu_q}} \tag{1}$$

$$\Delta f_{\text{non-rigid}} = -\frac{2f_0\Delta m}{A\sqrt{\rho_q\mu_q}} - f_0^{2/3}\sqrt{\frac{\rho_L\mu_L}{\pi\rho_q\mu_q}} \tag{2}$$

As mentioned above, the hygroscopic material plays a key part in the performance of QCM humidity sensors. There are several types of hygroscopic materials used for QCM humidity sensors. The most common are metal oxides [7] and polymers [8]. Unfortunately, a few researchers have noticed that some metal oxide- and polymer-based QCM humidity sensors suffer from anomalies in the frequency response in high humidity situations. For

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example, Dong observed that polymer based QCM humidity sensors appeared to have a reversal in their frequency response in high humidity situations [6]. Erol experimentally showed that ZnO-based QCM humidity sensors displayed a complete positive frequency response that goes against the basic relationship shown in Eq. (2) over the entire RH range tested [9]. The aforementioned experimental phenomena can be attributed to variations in the viscosity of non-rigid hygroscopic materials (especially the low stiffness of hygroscopic materials) due to extensive water adsorption. As the amount of absorbed water gradually increases, the enormous increase in viscosity of a non-rigid hygroscopic material will dampen the QCM, i.e., reduce the stability. Thus, for QCM humidity sensors, the hygroscopic materials not only affect the response according to Eq. (2) but also influence the sensor's stability.

In the last two decades, carbon nanomaterials have attracted growing interests in the fields of materials and physics because of their excellent electrical, mechanical and thermal properties. In the field of gas/humidity sensor technology, carbon nanomaterials have also been considered to be very promising materials because of these properties and their outstanding molecular adsorption capacity. Up to now, various types of carbon allotropes, such as fullerene [10], carbon nanotubes [11] and graphene [12], have been used as gas/humidity sensitive materials. In 2005, Goyal found that using a QCM with a carbon nanotube coating can significantly improve its frequency stability [13]. The reason for this stability improvement can be attributed to the high stiffness provided by carbon nanotubes. This finding opens a new door to develop high stability QCM sensors by using high stiffness, sensitive materials. Graphene, the thinnest known material in the universe and the strongest ever measured, has also caught the eyes of gas/humidity sensor researchers. Similar to other carbon nanomaterials, graphene can provide tremendous specific surface areas and a large number of active adsorption sites. However, the intrinsic hydrophobic property of graphene limits its use in humidity sensors [14,15]. To solve this problem, pioneering works have been carried out to enhance the hydrophilic nature of graphene by the functionalization of graphene with hydrophilic groups. For example, Lin prepared graphene/TiO_2 composites and studied their humidity sensing properties [16]. In these composites, TiO_2 materials were used to increase the number of water adsorption sites and the graphene material was used to increase the specific surface area. Our previous work found that graphene oxide (GO), as one of the most important graphene derivatives, was a promising hygroscopic material for preparing a QCM humidity sensor [17]. Zhao fabricated a CMOS interdigital capacitive humidity sensor by using GO films as humidity sensing films [18]. Our group proposed a stress-type humidity sensor by using GO-silicon bi-layered structure [19]. Balashov fabricated SAW humidity sensor by drop-casting GO suspension on SAW substrate [20]. Borini utilized GO films to prepare an ultrafast resistive-type humidity sensor [21]. Su experimentally studied the humidity-sensing properties of reduced GO thin film on a flexible substrate [15]. Zhang fabricated GO based resistive humidity sensor by using a layer-by-layer self-assembly method [22]. It is noticeable that the oxygen content of GO materials used in these above work is a fixed value. As is known, GO can be viewed as functionalized graphene with oxygen functional groups attached to the carbon sheet. In addition to the high stiffness and large specific surface area, the water adsorption capacity of GO is enhanced due to the introduction of oxygen functional groups. As such, we can see that the oxygen content of GO is an important parameter to determine the sensor's performance because it directly determines the water adsorption capacity. In this work, we prepared a series of QCM humidity sensors that utilize GO materials with different oxygen contents. The influence of the oxygen content in the GO hygroscopic material on the humidity sensing performance of the QCM humidity sensors, such as humidity response and stability, humidity hysteresis, dynamic response and recovery, will be discussed.

2. Experimental

2.1. Preparation of GO dispersions with different oxygen content

As described by Krishnamoorthy [23], the oxygen content of graphite oxide can be adjusted by controlling the added amount of $KMnO_4$ powder. In this work, graphite oxide with different oxygen contents was synthesized by graphite oxidation with a certain amount of $KMnO_4$ in concentrated H_2SO_4. Briefly, 5 g of graphite powder was placed in cold (0 °C), concentrated H_2SO_4 (115 mL). The required amount of $KMnO_4$ was gradually added to the mixture by mechanical stirring and cooling to keep the temperature of the mixture below 20 °C. Then, the mixture was stirred at 35 °C for 1 h and diluted with 230 mL of distilled water while stirring vigorously. Seventy milliliters of distilled water and 50 mL of a 30% H_2O_2 solution were added, and the reaction was terminated after 15 min. Finally, the mixture was filtered and washed with a 5% HCl aqueous solution completely until the pH of the rinse water became neutral, and then, the GO was obtained after drying. In this experiment, three GO samples with different oxygen contents were prepared by varying the amount of $KMnO_4$ added (5 g, 10 g and 15 g) and were named GO-1, GO-2 and GO-3, respectively. Single-layered GO nanosheets were subsequently obtained by exfoliating graphite oxide with ultrasonication in water using an ultrasonic bath (KQ-300DE, 300 W, 40 kHz) for 1 h. The concentration of the prepared GO dispersions was 1 mg/mL.

2.2. Fabrication of GO based QCM humidity sensors

AT-cut QCM transducers (10 MHz) with 5-mm diameter electrodes were purchased from Wuhan Hitrusty Electronics Co. Ltd., China. Before fabricating the humidity sensors, all of the QCM transducers were rinsed with deionized water and ethanol repeatedly to remove pollutants and then dried in oven for 6 h at 40 °C. Then, 2 μL of the GO dispersions of the different oxygen contents were drop-cast on the surface of the devices to cover the whole electrode of the QCM transducer. After evaporating the water in a drying basin at room temperature for 6 h, the fabrication of a series of QCM humidity sensors with different oxygen content of the GO membrane was complete. By using Sauerbrey relationship as shown in Eq. (1), we can calculate the thickness of GO films on the QCM. The calculated thickness is about in the range of 110–150 nm. The sensors were denoted as S1, S2 and S3 according to the oxygen content of the GO sensitive film from low to high.

2.3. Measurements

A schematic diagram of the experimental setup is shown in Fig. 1. It consists of several standard humidity sources and some measuring equipment. Saturated LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KNO_3 and K_2SO_4 solutions were used to yield 11.3%, 32.8%, 54.3%, 75.3%, 93.5% and 97.3% humidity levels, respectively. A commercial phase lock loop oscillator (Plo-10i, Maxtek) was used to drive the QCM sensor, and the frequency output was recorded by a frequency counter (53131A, Agilent) in real time. The oscillating circuit method only provided the resonance frequency information and did not give the stability information of the QCM. For this reason, a precision impedance analyzer (6500, Wayne Kerr) was also used to acquire the electro-acoustic parameters of the QCM humidity sensor near its resonance at different RH levels. Compared with a classical oscillating circuit, the impedance analyzer