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A humidity sensor based on quartz crystal microbalance using graphene oxide as a sensitive layer

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A B S T R A C T

Humidity is a vital physical quantity which is extremely important to production quality control, reliability of electronics, and health of human being. This paper proposed a humidity sensor based on quartz crystal microbalance (QCM) using graphene oxide as a sensitive layer, and investigated the characteristics of sensor according to the shift of quality factor (Q factor) as well as resonant frequency at different relative humidity (RH). Results show that at low RH values, the shift of Q factor is more suitable than the shift of resonant frequency for assessing the sensitivity of the sensor. By combining both frequency and Q factor shifts, we obtain a sensitivity of ~1371/1%RH at 10–60%RH (by Q factor) and 1068 Hz/10%RH at 70% RH (by frequency), which are much better than the reported QCM humidity sensors, with good linearity. The QCM humidity sensor also shows good repeatability with response time and recovery time smaller than 20 and 3 s, respectively. These good characteristics of the sensor are attributed to the large surface area and high hydrophilic nature of the graphene oxide, demonstrated good potential for future applications.

1. Introduction

Humidity is a vital physical quantity strongly related to human's activities and daily lives. It must be measured and controlled in many fields such as production lines, agriculture, meteorology, and space flight. Relative humidity (RH) is the most commonly used parameter, which is defined as the ratio of the partial pressure of water vapor to the equilibrium vapor pressure of water at the same temperature and pressure. Various mechanisms have been utilized to develop humidity sensors with some of them being commercialized. Among them, humidity sensors based on resistance or capacitance change induced by humidity variation are very popular due to their simple detection methods and relatively high measurement precision [1] [2]. However, the yield and reliability of both resistance-typed and capacitance-type humidity sensors are very low. Recently, Quartz crystal microbalance (QCM) humidity sensor has received much attention due to its high sensitivity, good repeatability, short response/recovery time and well-established manufacturing and measurement technologies. QCM device was first proposed by Sauerbrey [3], who demonstrated that AT-cut of piezoelectric quartz crystal can be treated as microbalance and developed a relationship between mass change and resonant frequency shift in 1959. The relationship can be expressed by equation (1):

$$\Delta f = -2f_0^2 \Delta m \Big/ A\left(\mu_q \rho_q\right)^{0.5} \tag{1}$$

where Δf is the change in resonant frequency of quartz crystal due to a mass load of Δm on the surface, f_0 the original resonant frequency, A the active area of crystal, ρ_q the density and μ_q the shear modulus of quartz. To sense humidity, QCM is typically coated with a sensitive or sensing layer, which absorbs different quantities of water vapor at different RH, leading to different mass loads. Radeva et al. used fullerene as the sensitive layers for QCM humidity sensor in 1997 [4], since then various nanomaterials have been used as

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sensitive layers in succession for humidity sensors as their large surface areas could enhance the sensitivity of sensors dramatically. Zhang et al. adopted carbon nanotubes as sensitive layers which were prepared by the spin coating method [5]. The sensitivity of the carbon nanotubes coated sensor was high and the response speed was around 1 min. Su et al. reported a QCM humidity sensor with a double-walled carbon nanotubes (DWNTs) sensitive layer [6], which was used in low humidity environment. Aziza et al. reported a graphene functionalized humidity sensor with good sensitivity, response/recovery, and repeatability [7]. Although carbon nanotubes and graphene flakes are good sensitive layers owing to their large surface areas, the certain degree of hydrophobicity nature of these carbon nanomaterials have suppressed their positive effects on sensitivity. On the other hand, graphene oxide (GO) flakes are a hydrophilic material beside the common nature of nanomaterials [8], and graphene oxide as a sensitive layer is expected to enhance the sensitivity of QCM humidity sensors significantly as demonstrated by flexible and transparent surface acoustic wave based humidity sensors [9]. Yao et al. first studied the humidity sensing characteristics of GO on QCM and obtained the relationship between frequency shift and RH [10]. We found that the quality factor (Q factor), which is a dimensionless parameter that indicates the energy losses within a resonant element and typically characterized by the frequency-to-bandwidth ratio of the resonator, of QCM is sensitive to RH as well. In this paper, we propose a QCM humidity sensor with GO as the sensitive layers, and investigate the sensitivity, repeatability, and response/recovery speed based on the analysis of both the shifts of resonant frequency and Q factor, demonstrating a good prospect in humidity sensing application.

2. Experiments

2.1. Manufacture processes

The proposed QCM humidity sensor used graphene oxide as the sensitive layer. Fig. 1(a) and (b) are the schematic view and photo of QCM with GO sensitive layer respectively. The QCMs without GO layer, consisting of a 166.5 μm thickness AT-cut quartz crystal sandwiched by two Au electrodes, were provided by Interquip Electronics Co. (Hong Kong, China) with a resonant frequency of 10 MHz. The processes of preparing a GO layer for QCM humidity sensor are as follows: First, the original QCM was washed successively in acetone (5 min), ethyl alcohol (5 min) and deionized water (3 min) by ultrasonic cleaning. Then, the QCM was dried by nitrogen gas, and baked at 60 °C for 10 min. The initial GO dispersion had a concentration of 2 mg/ml, and it was diluted by deionized water at a ratio of 1:40. A GO sensitive layer was deposited on the surface of the Au electrode of the QCM with the thickness of approximately 400 nm by dispensing GO solution drops on the surface and dried in air at room temperature. After the GO solution on electrode dried out, we obtained a QCM humidity sensor with a GO sensitive layer. The thickness of GO layer was measured by the profilometer (Veeco Dektak 150) as shown in our previous paper [11].

Instead of using a commercial QCM measurement setup, we

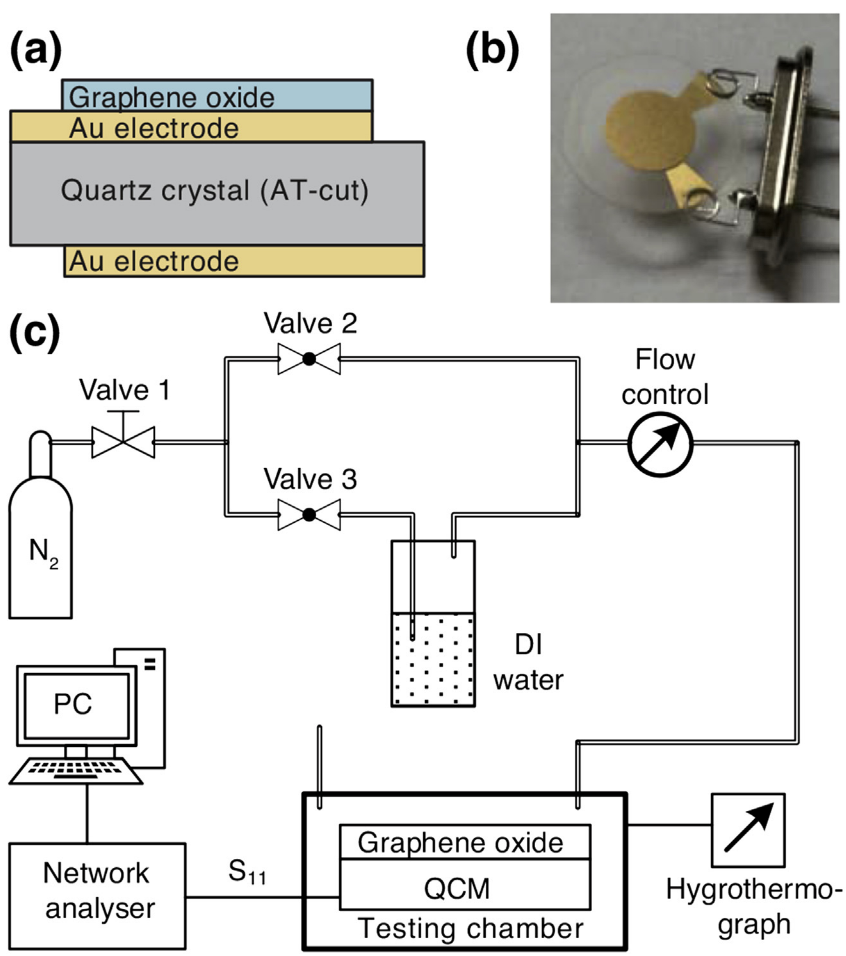

Fig. 1. (a) Cross-section schematic view and (b) photo of QCM with GO layer; (c) schematic view of the testing system used for humidity sensing.

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