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Correlation between the sensitivity and the hysteresis of humidity sensors based on graphene oxides

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ABSTRACT

We report on the correlation between the sensitivity and the sorption/desorption hysteresis of thin-film humidity sensors based on graphene oxides (GO). Both properties are systematically investigated by the conductance change of thin-film humidity sensors as well as the resonance frequency shift of quartz crystals coated with GO with varied pH. GO-based humidity sensors made at pH 3.3 present a lower level of sensitivity (2.1 ± 0.4 μS/%RH) and hysteresis-induced error (2.8 ± 0.1%RH) whereas those made at pH 9.5 present an increased level in both sensitivity (12.3 ± 2.2 μS/%RH) and hysteresis-induced error (3.7 ± 0.6%RH) by conductance measurements in the humidity range from 10%RH to 90%RH. Such correlation between two properties is also observed when the thickness and the functionality of GO films are varied. The correlation in GO-based humidity sensors is consistent with the correlation determined by a quartz crystal microbalance, indicating that the actual change of the water content in GO films underlies such behaviour. We discuss a possible mechanism for the observed correlation between the sensitivity and the hysteresis based on charged states on GO surface and their interactions with water molecules by using Fourier transform infrared (FT-IR) spectroscopy, water contact angle measurements, and response/recovery time measurement. Our findings would provide a new insight for the development of humidity sensors based on GO and its derivatives.

1. Introduction

Humidity sensors are useful for monitoring living environments as well as for quality control in various industries, for example, food, timber, weather, chemistry, and semiconductor [1,2]. For the development of humidity sensors, sensing properties such as sensitivity, response time, hysteresis, stability, and humidity detection range should be tested to meet specific needs from each industry. In general, polymers and metal oxides are utilized as a humidity sensing layer in most cases of commercial thin-film humidity sensors [3–5]. Recently, carbon-based materials including carbon nanotube and graphene have shown a promise for applications of gas and humidity sensors [6–11] owing to their unique electrical and chemical properties [12]. Among these materials, humidity sensors using graphene oxides (GO) have been demonstrated to have superior performances such as ultrahigh sensitivity [13], ultrafast response time [14], and flexibility [14,15]. However, most of thin-film humidity sensors including GO-based sensors suffer from hysteresis during sorption and desorption of water [15–18]. Even though hysteresis reduces the measurement accuracy due to a slight difference between sorption and desorption curves as a function of humidity, the hysteretic behaviour of humidity sensors has been paid less attention than other sensing properties. In this regards, systematic studies on the hysteresis and its correlation with other properties will be beneficial for better understanding sensor characteristics and thus for the development of new humidity sensors based on GO and its derivatives.

One of the efficient ways to change material properties is to adjust pH. Previously, it is reported that charged states of GO are significantly affected by changing the pH of the GO solution [19,20]. Specifically, carboxylic groups (COOH) on GO are dissociated into carboxylate anions (COO^-) as pH is increased ($pK_a = 6.6$) and the phenolic/hydroxyl groups (C—OH) are also ionized into phenolate anions ($C—O^-$) as the pH is further raised ($pK_a = 9.8$) [20]. Consequently, some visible properties of GO such as dispersibility and photoluminescence are shown to change depending on the charged state of GO. In addition to the pH adjustment, one of the practical methods to control the surface state of GO is thermal treatment.

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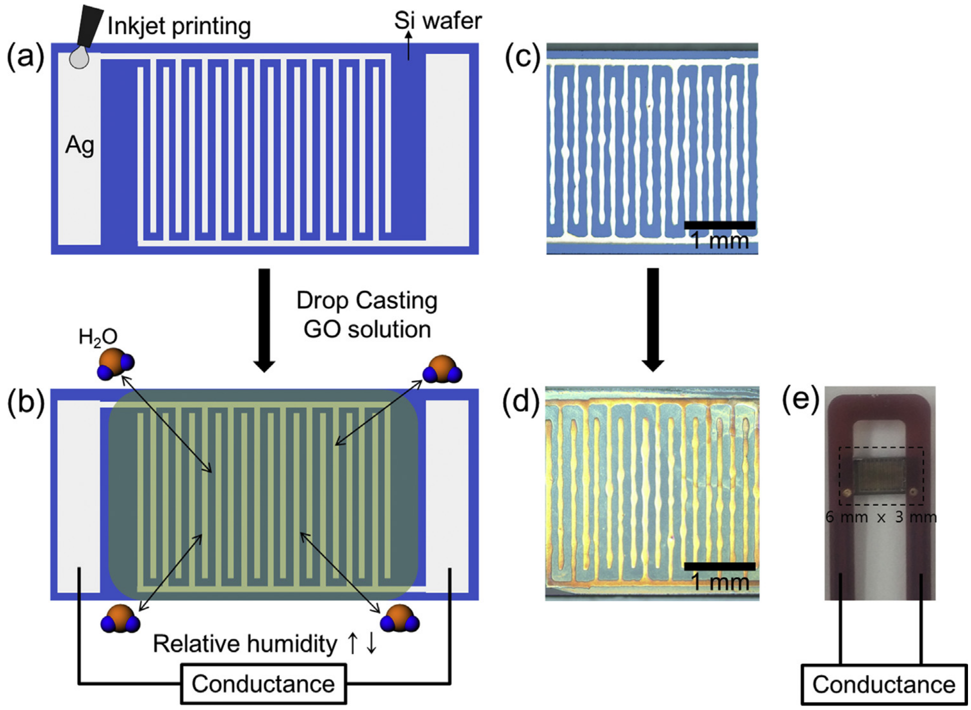

Fig. 1. Schematic diagrams of (a) interdigitated sensor electrodes fabricated through inkjet printing of silver nanoparticles and (b) the humidity sensing layer through drop-casting of graphene oxides (GO) followed by the measurement of relative humidity via conductance. Micrographs of (c) fabricated electrodes and (d) the GO film on the substrate. (e) Photograph of the prototype of the GO-based humidity sensor attached to the sensor boom.

Thermal treatment at high temperature (>1000 °C) leads to the reduction of GO in which oxygen groups are significantly decreased [21]. Moreover, a stepwise reduction of GO has been demonstrated in which epoxide (C—O—C) and hydroxyl (C—OH) groups is sequentially removed by using the combination of chemical and thermal reduction, respectively [22,23]. Moreover, the functionalization of GO with various materials such as polymers, nanoparticles, and organic compounds has been introduced for sensing applications in many fields [24]. In this regard, it will be interesting to study on how humidity sensing properties of GO are changed depending on its surface states that can significantly affect the interaction of water molecules with GO.

Here, we report on the correlation between the sensitivity and the hysteresis of humidity sensors based on GO as a humidity sensing material. The degree of hysteresis in GO-based sensors is represented by the hysteresis-induced error and then its correlation with the sensitivity is studied with varying the pH of GO. As the pH of GO solution is raised, both the sensitivity and the hysteresis-induced error are increased in the conductance measurement of thin-film humidity sensors as well as in the resonance frequency measurement using a quartz crystal microbalance (QCM). The mechanism of the observed correlation between two properties is discussed on the basis of charged states of GO and its interactions with water by using water contact angle measurements and Fourier transform infrared (FT-IR) spectroscopy. The present study provides a useful insight for understanding sensing characteristics of humidity sensors and especially for the development of humidity sensors based on GO and its derivatives.

2. Material and methods

2.1. Materials

For the fabrication of sensor electrodes, inkjet printing technique is applied using a silver (Ag) nanoparticle solution (Advanced Nano Products, Korea) on Si wafer (Namkang Hitech Co., Korea) having a SiO_2 layer (100 nm in thickness). Graphene oxide (GO) used as a humidity sensing material is prepared from graphite flake (Aldrich) by modified Hummers method [25]. Detailed method for the synthesis of GO is summarized in Supplementary material.

2.2. Fabrication of GO-based humidity sensors

Electrodes for humidity sensors are fabricated through inkjet printing (DMP-2831, Fujifilm, USA) using a silver (Ag) nanoparticle solution on the pre-cut Si wafer (6 mm × 3 mm in dimension) as schematically shown in Fig. 1a. The operating temperature of the printer substrate, where target Si wafer is located, is maintained at 60 °C while printing. When the printed Ag solution is fully dried on the Si wafer, it is thermally treated at 400 °C for 2 h for the enhancement of conductivity. GO is dispersed in deionized (DI) water to a concentration of 1 mg/ml and filtered through a membrane having 5 μm pores before use. The pH of GO solutions is adjusted to desired values using 0.1 M HCl or 0.1 M NaOH. The humidity sensing layer is formed through drop-casting (10 μ*l*) of the prepared GO solution on the sensor substrate with electrodes. Then, the GO solution is allowed to dry at room temperature. The performance of humidity sensors is tested by conductance measurements at varying relative humidity as schematically shown in Fig. 1b. The printed Ag electrodes on the Si wafer and the GO film coated on the sensor substrate are shown in Fig. 1c and d, respectively. The fabricated GO-based humidity sensor is attached to a sensor boom to facilitate the conductance measurement at varying humidity as shown in Fig. 1e.

2.3. Generation of relative humidity and humidity measurements

For the generation of desired relative humidity (%RH in unit), a divided-flow-type humidity generator submerged in a thermostatic bath is used as shown in Fig. S1. Desired humidity inside the test chamber where the GO-based humidity sensor is positioned is obtained by controlling the flow rate of 0%RH ($F_{0\%RH}$) and 100%RH