Swelling characteristics and application of two-dimensional materials on hydrophilic quartz crystal resonant dew point sensor

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\textbf{ARTICLE INFO}

\textbf{Keywords:}
Two-dimensional materials
Montmorillonite
Graphene oxide
Molybdenum disulfide
Dew point sensor
Quartz crystal resonant

\textbf{ABSTRACT}

The two-dimensional (2D) water adsorbing material is used as a sensitive layer for the hydrophilic quartz crystal resonant (QCR) dew point sensor, and its own swelling characteristics determine the accuracy of the sensor's recognition of the saturation status of the water vapor. In order to reveal the mechanism relationship between the swelling characteristics of materials and the measurement accuracy of hydrophilic QCR dew point sensors using different 2D materials, we used montmorillonite (MTT), graphene oxide (GO) and molybdenum disulfide (MoS\textsubscript{2}) coated QCR sensors to test dew point measurement performance in different humidity environment, and then the rate of swelling and intensity of swelling of the three materials were measured by integration of quartz crystal microbalance with dissipation (QCM-D) and ellipsometer. The results showed that MTT had an outstanding swelling rate and intensity with logarithmic thickness changing curve, especially in the high humidity environment with sudden strength changes. This characteristic makes MTT the most suitable sensitive material for the hydrophilic QCR dew point sensor surface modification among the three 2D materials. Through this study, it implied that the rate of swelling and intensity of swelling are the two major parameters that determines whether a 2D material is suitable for being used as the sensitivity layer of a hydrophilic QCR dew point sensor.

\section{1. Introduction}

The dew point measurement is widely known as the most accurate method for measuring humidity \cite{1}. The main high precision dew point measurement methods are cold mirror photoelectric method and quartz crystal resonant (QCR) dew point measurement method. Both methods use active temperature control to generate moisture condensation and then directly measure the temperature at the time of water vapor saturation. Among them, the cold mirror photoelectric method has developed into a mature product, which has been widely used as a standard instrument. QCR dew point sensor has a core problem to be solved in the process of instrumented research and development, it needs a unique characteristic parameter as the feedback of dew point tracking. However, due to the influence of temperature frequency characteristics (TFC) and external interference to frequency measurement in the actual test process, it is difficult to obtain the unique reliable characteristic parameter. Therefore, it is difficult to derive a mature and reliable instrument from QCR dew point measurement method. To this end, we have previously proposed a hydrophilic QCR dew point measurement method \cite{2}. By spraying two-dimensional (2D) adsorption material on the QCR electrode, the swelling characteristics of 2D material can be used to identify the time of water vapor saturation and eliminate the influence of TFC. This method can provide the unique reliable characteristic feedback parameter for the subsequent dew point automatic tracking system. Due to the different swelling characteristics of different materials, the measurement results obtained in the hydrophilic QCR dew point sensor are also different. Therefore, it is necessary to study the mechanism between material swelling characteristics and the performance of hydrophilic QCR dew point sensors.

2D materials exhibit great potential for humidity sensing applications due to the fact that almost all atoms are at the surface. Like sponge, when absorbing water, hydrosopic materials will have net volume increase as most of the water molecules are being sucked inside the nanochannel. However, for 2D materials, thickness increment is

\url{https://doi.org/10.1016/j.snb.2019.126905}

Received 16 June 2019; Received in revised form 29 July 2019; Accepted 29 July 2019
Available online 30 July 2019

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more obvious and presentable than volume gain, since 2D material will largely expand on axial direction but slightly on horizontal direction. This is because 2D materials have layered structure very similar to a stack of paper, and each stacked layer will tend to move vertically when volume is increasing. The thickness increment also refers to material swelling. Take GO as an example, when hydrated in water, it tends to deprotonate and carry negative charge on each stacked layer and the repulsion force overcomes the van der Waals attraction and hydrogen bonding attraction forces, resulting in separation of stacked layers [3]. Therefore, although many studies demonstrated extraordinarily steady and durable GO film [4,5], many other researches showed instable and redispersion of GO in aqueous environment [6–8].

In this work, the chosen three materials - MTT, GO and MoS2 all have distinctive swelling behaviors. Materials swelling will be characterized by integrating quartz crystal microbalance with dissipation (QCM-D) and ellipsometer to dynamically monitor the material swelling behavior. We will compare the swelling rate and intensity of these three materials to get a hint of how these two parameters contribute to the improvement for hydrophilic QCR dew point sensor.

2. Experimental

2.1. Principle of dew point identification

In this works, a hydrophilic QCR dew point sensor with different water absorbing material coating in combination with a smart dew point recognition algorithm have been successfully demonstrated. These moisture absorption coatings can reach saturation states as identified by the signal processing algorithm with minimum influences of the environment temperature [2]. The working principle is shown in Fig. 1. The selected 2D material was sprayed on the surface of the QCR electrode by air spraying technology, and then combined with the Peltier cooler as a sensitive unit. As the temperature drops, the air humidity on the surface of the material continues to decrease until it becomes saturated. The frequency of QCR will shift due to the continuous adsorption of water molecules by the material. Fourier fitting and second derivative of the frequency curve are used to identify the water saturation of the material surface and measure the dew point. Due to the difference of swelling speed and intensity, the saturation time of water vapor reflected by each kind of 2D material is different, which leads to the different measurement accuracy of the sensor.

2.2. Dew point sensing system

The sensor uses the symmetrical structure of double cooling and double contact surfaces which has high cooling efficiency and large gas/humidity contact areas [9]. As shown in Fig. 2(a), the QCR is fixed by two copper pillars which are also used for the transmittal of temperature and electricity. Two thermal gaskets are placed on either side of the QCR to transfer the heat from the copper pillar to the QCR surface and to isolate the transmission of the electricity. The graphite gasket is used for the transmission of both heat and electricity. Two platinum resistance thermometers (PT100) are embedded in the copper pillars to record the temperature and the average value is used as the temperature of the QCR surface during the experiment. Two Peltier coolers are placed on the either sides of the structure for cooling the QCR to the dew point temperature. Heat sinks are attached to the hot side of each Peltier cooler to improve the cooling efficiency. The outer covering is made of Polytetrafluoroethylene (PTFE) to reduce the effects of the environment temperature. The experiment system as shown in Fig. 2(b) included the sensor, the dew point generation system, the dew point measurement system and the dew point calibration system. In this work, the environment temperature had a range from 22°C to 23°C and the pressure of the measurement environment was 101 kPa, while the value of the gas flow rate was set at 0.5 L/min.

The dew point generating system consists of two dry gas tanks, one of which is connected to a humidifier, and the ratio of dry and wet air can be controlled by two micro-flow controllers to change the air humidity. The dew point measurement system contained the Agilent 4294A, the temperature control module, the temperature collection...
module, and a computer (PC). The Agilent 4294A was used to drive the QCR and transmit the frequency variations to the PC. The temperature control module controlled the temperature of the QCR by adjusting the input current of the Peltier cooler. In the experiments, the initial value of the input current was 0.5 A and the variation rate was 0.005 A/s, with a max value at 2 A. The temperature collection module recorded the temperature by collecting the resistance values of the PT100. The precise dew point gauge MICHELL S4000 was used as the standard dew point gauge. The gas with different dew point can go through MICHELL S4000 and the sensor in parallel during the measurement process.

2.3. QCM-D/Ellipsometry measurement for material swelling

Similar to one of our previous study [10], material swelling was characterized by QCM-D and ellipsometry to dynamically monitor the stacked nanosheets mass and thickness change during the water adsorption period and indirectly quantify the material density and d-spacing. Viscoelastic model is used for mass modeling and Cauchy model is used for thickness modeling, with wavelength at 633 nm. QCM-D is a device that measurement the nano-level mass change of a designated area on top of the resonating gold sensor, while ellipsometry is used for measuring the thickness change of a designated area through the polarization of light reflection. By integrating the mass change and thickness change data, we can compare the material rate of swelling and swelling intensity for each of the materials.

Three different solutions are prepared for vacuum filtration: 1. GO water dispersion (0.4 wt% concentration, Graphenea, Cambridge, MA, USA); 2. MoS2 water dispersion (170 ppm, prepared in lab same procedure as in one of our previous study [11]); 3. MTT water solution (4 mg/ml, direct sonication of clay in water). A polyester sulfone membrane (PES, Hydranautics, Oceanside, CA, USA) was used to be the membrane substrate for vacuum filtration. After the 2D materials are deposited onto the substrate, the QCM-D gold sensor is pressed against the freshly prepared thin film and peeled off from the substrate to coat a uniform 2D material film on gold sensor. This sensor is dried in oven for 12 h at 60 °C before measurement. The mass and thickness baseline of the gold sensor is collected before thin film coating. Subsequently, the oven-dried gold sensor with a thin film on top is again put in QCM-D/ellipsometer testing chamber, where moist air with different humidity (33%RH, 50%RH and 99%RH) is being pumped and get in contact with the thin film material one at a time. During the material water adsorbing period, QCM-D and ellipsometer is simultaneously measuring the mass and thickness change over time with respect to the baseline. By integrating the mass and density data, we can derive the d-spacing change and material density change over time (Fig. 3).

3. Results and discussion

3.1. Material characterization

According to X-ray diffraction (XRD) result, three dry samples have different d-spacing at about 0.32 nm (MTT, 2θ = 33.0), 0.4 nm (GO, 2θ = 26.4) and 0.63 nm (MoS2, 2θ = 16.5) respectively (Fig. 4). According to the XRD result, material ranks from large d-spacing to small d-spacing is MoS2, GO and MTT. All three materials have sharp signature peak, meaning that the materials all have good crystal alignment.
3.2 Sensor performance and material swelling behavior

Three humidity environments were selected to test the performance of three sensors with different material coatings. Fig. 5 shows the measurement results of the sensor with MTT coating sprayed on both electrodes in three humidity environments. The dew point values of the three humidity environments are 5.41°C DP, 11.57°C DP and 20.6°C DP, respectively. They correspond to low humidity, medium humidity and high humidity. Fig. 5(a) is the frequency output value of the sensor with MTT coating under the three standard dew points. It can be seen from the results that the frequency value decreases monotonously with cooling, but it is difficult to identify from the results that the material on electrode reaches saturation. Fig. 5(b) and (c) are the results of processing the three curves in Fig. 5(a) by Fourier fitting and second derivative respectively. We take the extreme inflection point of the curve as the identification point of the dew point and compare the measurement results with the standard dew point. The relative errors under three humidity conditions are 0.2°C DP, 0.34°C DP and 0.33°C DP, respectively. The measurement results are very satisfactory.

We also tested the sensors with GO coating and MoS2 coating in the same way, and the results are shown in Fig. 6 and Fig. 7 respectively. As can be seen from the results in Fig. 6, the relative measurement errors of the sensor with GO coating are 1.31°C DP, 1.06°C DP and 0.68°C DP, respectively. The measurement errors are larger than those of the sensor with MTT coating. The results in Fig. 7 show that the relative measurement errors of the sensor with MoS2 coating are 1.54°C DP, 1.47°C DP and 0.96°C DP, respectively. The measurement errors are generally larger than those of the sensor with GO coating. From the results of the three sensors, it can be found that the measurement accuracy of the sensor with MTT coating is the highest. In other words, the swelling strength and rate of the MTT material can best reflect the phase change of the electrode surface. In order to reveal the internal mechanism between the swelling characteristics of materials and the accuracy of dew point identification, three kinds of materials were tested under different humidity conditions. The relative humidity values of the three humidity environments are 33%RH, 50%RH and 99% RH, respectively.

According to QCM-D and ellipsometer result, the mass and thickness of three materials under different concentration of humidity air environment were measured. According to Fig. 8(a) and (b), the 43-nm dry MTT film is having mass at about 5000 ng/cm² before getting in contact with water molecules, which gives the dry MTT film density at 1.16 g/cm³. In low and medium humidity environment (33% and 50%), MTT thin film seemed not swell much as the thickness only increased for about 10% to about 50 nm in both cases. However, when humidity goes up to 99%, material swell intensively (thickness increased 50%–65 nm) and absorb great amount of water (mass increased to 7000 ng/cm²), reaching a final swelled density of 1.07 g/cm³. This phenomenon demonstrated that MTT has capability of absorbing water molecule and swelling intensively under high moisture content.
The thickness change curve is in logarithmic shape with initial steep slope and gradually decreasing to zero. Most of the swelling happened at the first 10 min. This also showed that MTT have good sensibility of water and short responding time under high moisture content.

According to Fig. 8 (c) and (d), the mass and thickness change of GO under different moisture content environment is demonstrated. At dry state, the 50 nm thick GO film is having mass at 10,000 ng/cm², meaning the density is at about 2 g/cm³. Unlike MTT, GO has a different and distinctive swelling behavior. In 33%, 50% and 99% humidity environment, GO film are gradually swelling with moderate intensity (thickness increased less than 5%). The shape of thickness change is close to polynomial. GO film is responding to water homogeneously and consistently no matter under what moisture content environment, as the shapes of thickness change are similar in 33%, 50% and 99% humidity environment. This result is like one of the previous studies [10].

Likewise, the mass and thickness change of MoS₂ thin film is recorded by QCM-D and ellipsometer as showed in Fig. 8 (e) and (f). Different from MTT and GO, MoS₂ thin film seemed do not swell conceivably under different moisture environment. The slope of thickness change is comparable to linear with no slope. This result agrees to one of the previous researches [11], validating the anti-swelling capability of MoS₂. In our result, the slight increase of thickness from 32 nm to 34 nm under 99% humidity environment might due to experimental error.

3.3. Discussion

Among these three materials, MTT is having highest swelling intensity according to previous studies, as the actual intensity of swelling normally lied within 100 Å [12-15]. However, according to literature, sodium-based MTT and calcium-based MTT have different swelling intensity [13,14,15]. Moreover, other parameters such as ionic concentration and surface charge density all play important role in MTT swelling [15]. In our study, we used a mixed MTT sample with both...
sodium-based and calcium-based components for QCR sensor surface modification. Secondly, GO has the intermediate tendency to swell. According to literature, a dry GO sample has d-spacing at about 0.8 nm while a hydrated and swelled GO sample has 6–7 nm interlayer space, giving a net void space increase at about 5–6 nm [10]. Lastly, MoS2 has the least tendency to swell with almost no swelling capability [11,16].

According to Fig. 9 (a), in 33% humidity environment, the thickness of MTT reached its maximum value very soon while GO is only gradually increasing and MoS2 is largely staying constant. The initial thickness of each material did not play an important role in the rate of swelling and intensity of swelling. The change of thickness in 50% and 99% humidity environment is similar as in 33% humidity environment (Fig. 9 (b)-(c)). These three materials all have distinctive swelling and water absorbing behaviors. The MTT logarithmic slope of thickness change, which is corresponding to the rate of absorption, is also larger than polynomial shaped GO and linear shaped MoS2 in the first 10 min. Combined with the three sensor accuracy performance results and the swelling characteristics of the three materials, it can be found that the rate of swelling and the intensity of swelling is the two key parameters that directly determine the accuracy of dew point identification. First, according to Fig. 9, MTT has faster rate of swelling than GO and MoS2. Secondly, MTT is also having higher intensity of water absorption than GO and MoS2, as the change of thickness of MTT is highest among all materials. For example, in 99% humidity environment, MTT swelled for about 50% while GO and MoS2 are less than 5%. Thirdly, the initial

Fig. 8. The results that measured by QCM-D coupled with ellipsometer for consecutive 40 min. (a), (c) and (e) are the mass of the MTT, GO, MoS2 thin film under dry, 33%, 50% and 99% humidity content environment; (b), (d) and (f) are the thickness of the MTT, GO, MoS2 thin film under dry, 33%, 50% and 99% humidity content environment.
material thickness does not significantly affect the rate of swelling. Based on the above characteristics, the swelling intensity of MTT shows an obvious abrupt change when the hygroscopicity reaches the critical saturation, resulting in the extreme inflection point in the results of the second derivative. However, the swelling intensity of the other two materials does not change significantly in the high humidity environment, so that the characteristics of the material at the moment of saturation are not obvious. The other two materials also have the extreme inflection point of the second derivative, which is caused by the phase change of moisture condensation after the hygroscopicity reaches the supersaturation. Therefore, MTT is the most suitable material based on the dew point identification method among the three materials. According to the analysis results, it can be concluded that materials with similar swelling characteristics to MTT are also suitable for this method. In addition, it is worth noting that according to the experimental results, it can be found that GO is the material with the fastest response to humidity among the three materials. However, due to the limitation of its own swelling intensity and rate, it does not show satisfactory recognition accuracy in this method. But in the field of relative humidity sensors, GO should be one of the better candidates.

4. Conclusion

In this work, we studied the mechanism relationship between the swelling characteristics of materials and the measurement accuracy of hydrophilic resonant dew point sensors using different 2D materials. We selected QCR sensitive components coated with MTT, GO and MoS2 and carried out dew point test experiment. Then, the swelling rate and intensity of the three materials were measured by QCM-D/ellipsometer. The results show that the measurement precision ranked from high to low is MTT, GO and MoS2. The intensity of swelling and the rate of swelling are the major factor of determining the precision of a surface modified dew point sensor. MTT has an outstanding rate of swelling and intensity of swelling, especially in the high humidity environment with sudden strength changes. This characteristic makes MTT the most suitable sensitive material for the hydrophilic resonant dew point sensor among the three 2D materials. Through this study, it can be generally concluded that which adsorption material can be used as the sensitive layer of the hydrophilic dew point sensor. Moreover, it is also verified that GO has a strong sensitivity as a hygroscopic material. Although it is not suitable to be used in hydrophilic resonant dew point sensor due to the limitation of swelling characteristics, it has a strong advantage in the application of relative humidity sensor.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (61603349); This project is also funded by Shenzhen Municipal Science and Technology Innovation Council of Shenzhen Government, China (JCYJ 20170818093844118) and Guangdong Provincial Natural Science Foundation of China (2018A030313984).

References

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