Influence of ZnO morphology on humidity sensing performance based on quartz crystal microbalance

Juan XIE¹², Hu WANG¹², Ming DUAN¹³ and Junlei TANG¹³

¹State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University (SWPU), Chengdu 610500, China
²The Center of New Energy Materials and Technology, School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, China
³College of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500, China

Two different morphologies of ZnO synthesized by hydrothermal method were coated on quartz crystal microbalance (QCM). Field emission scanning electron microscopy and X-ray diffraction were used to analyze the morphology and crystal structure of ZnO. The humidity sensing behavior was examined by measuring the resonance frequency shifts of QCM in the whole humidity range from 11 to 95%. The kinetics of adsorption–desorption and mechanism of humidity sensing were studied. The results show that the morphology of ZnO greatly affects the humidity sensitivity of QCM sensor. Furthermore, the adsorption–desorption model is also dependent on the morphology of ZnO.

©2018 The Ceramic Society of Japan. All rights reserved.

Key-words: Quartz crystal microbalance (QCM), ZnO, Hydrothermal method, Humidity sensor, Morphology

1. Introduction

Humidity sensors have been playing an increasingly important role in various fields, such as industrial production, food storage, electric appliances, automobile industry, environment monitoring and protection, and so on.¹–³ The quartz crystal microbalance (QCM) is an extremely stable and powerful device, which can be highly sensitive to mass changes on the nanogram scale.⁴ Therefore, an increasing number of researchers have generally come to recognize the wisdom of using QCM as a promising technology to improve upon reliable and highly sensitive humidity sensors.⁵–⁹ Sensing materials coated on QCM contribute a lot to promoting the sensitivities of humidity sensors.

At present, different sensing materials have been developed as the coating films to detect humidity. These materials include polymers, metals, ceramic oxides and carbon absorption materials.¹⁰–¹⁵ Sensor parameters such as sensitivity, response time, and recovery time are strongly dependent on the kinds of sensing materials. A variety of ceramic oxides have been regarded as one of the most important types of sensing materials in the past decades. These classical materials include ZnO, SnO₂, In₂O₃, CdO, et al., which present excellent sensing properties, like high sensitivity, fast response and recovery, good stability.

However, the importance of morphology of the coating film can never be overestimated. We found that the ZnO with different morphologies could exhibit different sensing properties.

In this paper, two different morphologies of ZnO were synthesized by the hydrothermal method on QCM wafers as humidity sensors. The humidity sensor was tested at room temperature by varying the relative humidity (RH) from 11 to 95%. These two different morphologies of ZnO behave rather different sensitive properties and kinetics. It is attributed to the morphology of the ZnO sensing film. The relationship between humidity sensing and morphology of ZnO was also discussed in this work.

2. Experimental

2.1 Fabrication of ZnO sensing film on QCM

All the chemicals were analytic grade reagents without further purification. The solvent medium used for the reaction system was distilled water. ZnO sensing materials were synthesized by the hydrothermal method. The aqueous precursor was prepared by zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O] and sodium hydroxide (NaOH), with the concentration of zinc ions and hydroxyl both being 0.2 mol/L, respectively. The mixture was transferred into a Teflon-lined stainless steel autoclave (capacity, 50 mL) with a filling capacity of about 30%. The autoclave was heated at 120°C for 8 h (labeled as S1) and 12 h (labeled as S2), respectively. After the experiments, certain volume
of suspension with white small particles was synthesized. 15 µL suspension was dropped onto the Au electrode of QCM wafers. Then the coatings were dried in a furnace at 80°C for 1 h. After evaporating the solvent, the white thin films were found on the surface of the QCM wafers.

2.2 Measurements

The morphology of the ZnO film on the QCM was observed with the field emission scanning electron microscope (FESEM, JSM-7500F). The crystallinity and crystal phases of as prepared samples were determined by X-ray diffraction (XRD, BEDE-DI, with Cu Kα radiation, λ = 0.5142 nm), with Bragg angle ranging from 20 to 85 deg.

A closed vessel partly filled with saturated salt solutions generates RH in the free room above the salt with good accuracy. The value of RH depends on the type of salt. Therefore, the controlled humidity environments were achieved with saturation aqueous solutions of LiCl, MgCl₂, Mg(NO₃)₂, NaCl, KCl, and KNO₃ in a closed glass vessel at ambient temperature, which yielded 11, 33, 55, 75, 85, 95% RH, respectively. Each of the saturated salt solution was kept in the glass chamber for 24 h before the measurement. The sensing properties were examined caused by the additional mass loading. The resonance frequencies were measured by a QCM digital controller (QCM200, Stanford Research Systems). The QCM sensors were suspended above a half-filled closed container without contacting the solution and they were stored in a dry environment after the test finished. The frequency signals were measured during the adsorption process (RH from 11% to other higher RH%) and desorption process (RH from other higher RH% to 11%).

3. Results and discussion

3.1 Characterization

The crystallographic morphology of ZnO can be influenced by many experimental parameters, such as basicity of the reaction system, precursor solvent, reaction time and temperature. In this paper, it is focused on the effect of the reaction time on the morphology of ZnO. Figure 1 shows the SEM images of the as-obtained ZnO crystals prepared with different reaction time. It can be seen in Fig. 1(a) that QCM wafer was coated with small particles (the size is smaller than 20 nm), while in Fig. 1(b) about 100 nm secondary particles are grown, which are made up of small particles. Compared to S2, the film of S1 is much smoother and more compact. The possible explanation to the different morphologies is that the growth of ZnO is divided into two stages. Firstly, nanoscale particles grow, which are joint together to form the smooth film. With the reaction time extending, these small particles grow gradually and cluster together in secondary particles.

As shown in Fig. 2, the XRD pattern of S1 and S2 was obtained. All the diffraction peaks can be indexed as the zincite phase ZnO reported in the standard card (89-7102). No obvious characteristic peaks are observed for other impurities. It is manifested from Fig. 2 that peak intensity of S1 is much stronger than that of S2. At the same time, the full width at half maximum of S1 is wider than that of S2. According to Scherrer equation, the size of particles of S1 is smaller than that of S2, which is consistent with the results of SEM.
3.2 Humidity sensitive property

Figure 3 describes the typical real-time frequency-response curves of the QCM sensor coated with ZnO exposed to different RH at room temperature, respectively. Frequency was recorded versus time till reached to the steady state and then the fully desorption of the sensor was obtained under 11% RH. Figure 3(a) shows the exposure of different RH to the based on S1 sensor. The frequency signal trace of the sensor based on S2 during intermitted exposure to RH conditions between 11 and 95% was plotted in Fig. 3(b). It can be also observed that from Fig. 3 that with increasing RH, both of the two samples seem to be difficult to establish the adsorption–desorption equilibrium. In other words, it will take more time to reach the equilibrium state under the higher RH.

Figure 4 illustrates the relationship between the frequency shifts and humidity ascending process of the two samples. It shows that the resonance frequency shift rose negatively with the increase of RH for the both samples. However, the frequency shift of S1 is much larger than that of S2 under the same humidity condition, indicating an increase in humidity sensitivity. As also can be seen from Fig. 4, the frequency shifts as a function of the RH do not indicate a linear tendency with increasing RH. The fitting linear equations of the two samples are \( Y = 1.648 + 0.015X \) and \( Y = 0.604 + 0.022X \), the coefficients of determination, \( R^2 \), are 0.974 and 0.994, respectively.

3.3 Kinetics and humidity sensing mechanism

The kinetics of the QCM sensor based on two different morphologies ZnO under humidity condition from 11 to 95% RH was studied. It is manifested from Fig. 5 that the derivative of frequency was plotted against time during the whole adsorption–desorption process. As shown in this figure, the negative peaks represent velocity of adsorption on the QCM sensor, while the positive peaks indicate velocity of desorption from the QCM sensor. With increasing of RH, the values of peaks rise. This result indicates that during exposure to high RH, the velocity of adsorption–desorption is relatively rapid. Certainly, both of positive and negative peaks intensity of S1 are much stronger than that of S2. It means that the velocities of adsorption and desorption of S1 are faster than that of S2. It implies that the morphology of S1 is more feasible to adsorb and desorb water molecules than that of S2. As described in Fig. 5(a), under the same humidity, the velocity of adsorption is quicker than that of desorption. Therefore, water molecules are more liable to adsorb on the surface of S1. Unlike S1, the adsorption velocity of S2 is faster than desorption only in lower humidity. On the contrary, under higher humidity, water molecules seem to be more inclined to desorb from the surface of S2.

According to Fig. 5, the relationship between the peak values and RH was plotted (shown in Fig. 6). As shown in Fig. 6(a), the derivative of frequency as a function of RH exhibits a linear tendency with increasing RH. The fitting linear equation is \( Y = -32.030 - 1.542X \), and the related coefficient (\( R^2 \)) is 0.994. It implies that adsorption of S1 is dependent on environment humidity. During the desorption process, the velocity of desorption increases with increasing of RH. Compared to adsorption, the velocity of desorption is relatively slow. As can be seen from Fig. 6(b) that the behavior of adsorption and desorption of

![Fig. 3. Response and recovery curves of QCM sensors from different relative humidity: (a) S1; (b) S2.](image)

![Fig. 4. Frequency shifts of QCM humidity sensors of S1 and S2. The dependence of the frequency shifts of sensor was inserted.](image)
S2 is very different from S1. Both in the adsorption and desorption process, peak values of frequency derivative do not exhibit a linear tendency with increasing of RH. The velocity of adsorption is faster than that of desorption in lower RH (below 55%). When RH reaches to above 75%, the velocity of desorption is faster than that of adsorption.

As mentioned above, a reasonable explanation of adsorption and desorption mechanism is described. The morphologies of the two samples play a significant role in representing their different behavior of adsorption and desorption. The smooth film made up of nanoscale particles is easier to adsorb water molecules. Furthermore, water molecules are not easy to desorb from the surface of the smooth film. However, there is so much space among the secondary particles. Thus, under the low RH, water molecules tend to adsorb on the surface of the secondary particles. While under the high RH, water molecules seem to easily desorb from the surface of these secondary particles.

4. Conclusions

In summary, two different morphologies of ZnO have been synthesized by hydrothermal method with different reaction time. These different morphologies of ZnO modified QCM wafers were used for detecting different relative humidity. The following conclusions can be drawn:

(1) The different morphologies correspond to two stages of ZnO growth. According to different reaction time, different morphologies of ZnO film can be obtained.

(2) The morphology of ZnO film contributes a lot to adsorption–desorption behavior. Nanoscale particles and smooth film tend to absorb water molecules, while water molecules favor desorbing from the surface film which is made up of relatively big particles and has so much space. In one word, the adsorption–desorption model depends on the morphology of ZnO film.

Acknowledgments  This work was financially supported by National Science Foundation of China (No. 51641108).

References