Available online at www.sciencedirect.com
SciVerse ScienceDirect
Ceramics International 39 (2013) 3621–3625
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Humidity sensing properties of ZnO colloid crystals coated on quartz crystal microbalance by the self-assembly method

Juan Xie[a,b,*], Hu Wang[a,**], Yuanhua Lin[b], Ying Zhou[b], Yuanpeng Wu[b]

[a]*State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University (SWPU), Chengdu 610500, China*
[b]*College of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, China*

Received 29 August 2012; received in revised form 10 October 2012; accepted 11 October 2012
Available online 22 October 2012

Abstract

ZnO colloid crystals were coated on quartz crystal microbalance (QCM) by the self-assembly method. Field emission scanning electron microscopy and X-ray diffraction were used to analyze the morphology and crystal structure of ZnO colloid crystals. The sensing behavior was examined by measuring the resonance frequency shifts of QCM. The device exhibits excellent humidity sensing properties in the whole humidity range from 11% to 95%, such as good linearity, fast response time and recovery time, excellent reliability, and long-term stability. We also discussed the adsorption and desorption of water molecules on ZnO colloid crystals at different humidity conditions.

Keywords: D. ZnO; Colloid crystal; Humidity sensing; Quartz crystal microbalance (QCM)

1. Introduction

Accurate and reliable measurement of humidity has become an important issue in various fields, such as automobile industry, semiconductor manufacturing, pharmaceutical industry, soil moisture monitoring, packaging, and food processing [1–3].

Several promising sensing techniques including field effect transistors (FET) [4], bulk acoustic wave (BAW) [5], surface acoustic wave (SAW) [6] and quartz crystal microbalance (QCM) [7–11] have been developed and applied to enhance the accuracy of humidity sensors. Among above various sensing technologies, the QCM is an extremely sensitive and powerful tool for monitoring mass changes in the nanogram scale. The mass change (Δm) on surface of the quartz crystal is calculated by using the Sauerbrey equation from the frequency change (Δf) [12]:

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\mu\rho}} \times \Delta m = -C \times \Delta m$$

where f_0 is the resonance frequency of the fundamental mode of the QCM crystal, A is the area of the gold disk coated onto the crystal, μ is the shear modulus of quartz, and ρ is the density of the crystal. The frequency shift is directly proportional to the adsorbed mass on the QCM with sensitive coating materials. Therefore, the use of QCM coated with sensitive materials has become an alternative approach for detecting low humidity. Many kinds of sensing materials were prepared on QCM wafer to detect humidity, including organic polymers, metal oxides, and porous inorganic/organic materials [13–20]. However, limit to our knowledge, no reports on QCM-based sensors with coating ZnO colloid crystals have been reported.

In this work, ZnO colloid crystals were fabricated by a self-assembly method on a QCM wafer as the humidity sensor. The morphology and crystal structure of ZnO colloid crystals were analyzed by emission scanning

*Corresponding author at: State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University (SWPU), Chengdu 610500, China. Tel./fax: +86 28 83037346.
**Corresponding author. Tel./fax: +86 28 83037346.
E-mail addresses: Jennyx99@126.com (J. Xie), Senty78@126.com (H. Wang).

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2012.10.190

electron microscopy and X-ray diffraction, respectively. Humidity sensing capabilities of the ZnO colloid crystals were investigated by QCM technique at room temperature by varying the relative humidity (RH) from 11% to 95%.

2. Experimental

2.1. Fabrication of ZnO colloid crystals on QCM

ZnO colloid crystals were synthesized by the self-assembly method. 0.01 mol Zinc acetate dihydrate was added into 100 ml diethylene glycol. This reaction solution was heated under 180 °C. After reaching the working temperature, precipitation of ZnO spheres occurred. The intermediate product was placed in a centrifuge. The polydisperse powder was discarded and the supernatant was used in the next step. A secondary reaction was then performed to produce the monodisperse ZnO spheres, which began in the same way as the primary reaction. Prior to reaching the working temperature, however, typically at 170 °C, some volume of the primary reaction supernatant was added into the solution. After reaching 180 °C, the reaction was stirred for several hours. When the heat source was removed, flask cooled to room temperature. The ZnO colloidal suspension was prepared and the size of the spheres varied inversely and monotonically with the amount of primary supernatant added.

The suspension was dropped onto the QCM wafers. Then the coatings were dried in a furnace at 80 °C for 1 h. After evaporating the organic solvent, the white films formed on the surface of the QCM wafers.

2.2. Measurements

The morphology of the ZnO films on the QCM was observed with the field emission scanning electron microscope (FESEM, JSM-7500F). The crystal structure of ZnO colloid crystals was characterized by X-ray diffraction (XRD, BEDE-DI, with Cu-Kα radiation, $\lambda = 1.542$ Å). The controlled humidity environments were achieved with saturation aqueous solutions of LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl, and KNO_3 in a closed glass vessel at room temperature, which yielded 11%, 33%, 55%, 75%, 85%, and 95% RH, respectively [21]. Each of the saturated salt solution was kept in the glass chamber for 24 h before the measurement. The sensing properties of the sensors to humidity were examined by measuring the resonance frequency shifts of QCM because of 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 runs. The frequency signals were measured during the adsorption process (RH from 11% to other RH %) and desorption process (RH from other RH % to 11%).

3. Results and discussion

3.1. Materials characterization

The FESEM image in Fig. 1 indicates that the average diameter of the colloid spheres is about 450 nm. It can be observed at the same time that the colloid sphere is composed of primary particles. Therefore, the ZnO colloid spheres are secondary particles. Fig. 2 shows the XRD pattern of the as-prepared colloid crystals. All the diffraction peaks can be indexed as the hexagonal phase ZnO reported in the standard card (JCPDS 36-1451). No obvious characteristic peaks are observed for other impurities.

3.2. Humidity sensing property

Fig. 3 describes the frequency shift (left) and the dependence of the frequency shifts of the sensor (right)

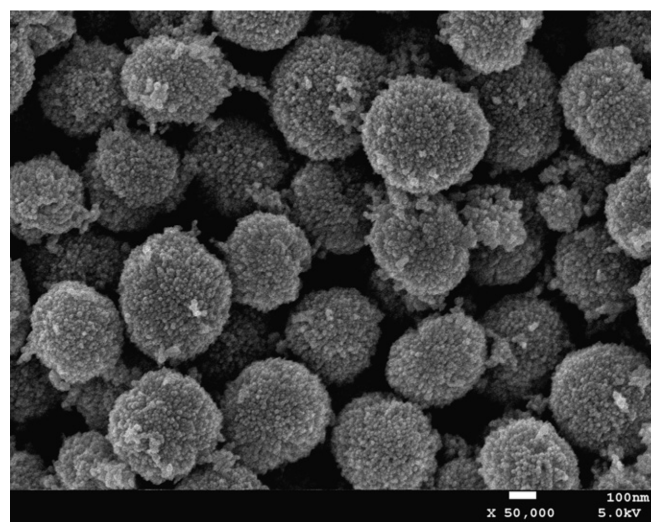

Fig. 1. Typical FESEM images of ZnO colloid crystals.

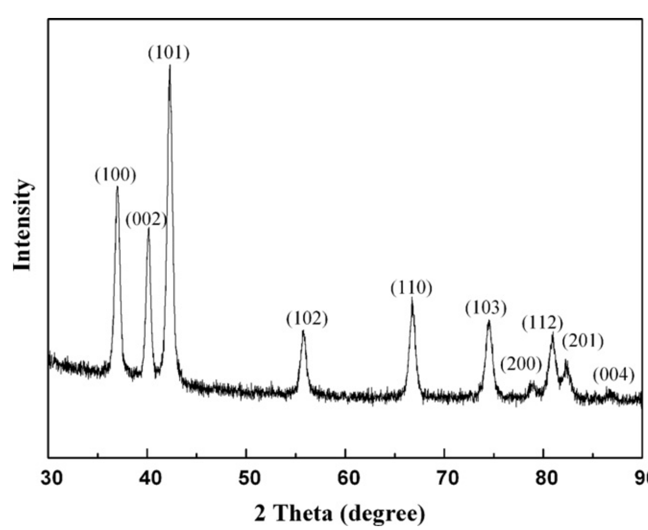

Fig. 2. XRD spectra of ZnO colloid crystals.