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# Capacitive humidity sensing properties of ZnO cauliflowers grown on silicon nanoporous pillar array

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ABSTRACT

Through growing zinc oxide (ZnO) on a template of silicon nanoporous pillar array (Si-NPA), a regular array of ZnO cauliflowers was prepared by a chemical vapor deposition method. All the cauliflowers were well separated and each cauliflower was composed of plenty of submicron-sized ZnO protrusions similar to undeveloped flower buds. The average diameter of the cauliflowers was ~3 μm. The flower buds sized from ~180 nm to ~350 nm and grown perpendicularly in local to the surface of the head. A capacitive humidity sensor was made based on ZnO/Si-NPA and its humidity sensing properties were investigated at 22 °C. A monotonous correspondence relation was found between the capacitance of ZnO/Si-NPA and the relative humidity (RH) of the measuring environment. With the RH changed from 11.3% to 94.6% and under a measuring frequency of 1 kHz, a capacitance increment over 21,400% was achieved, from 6.62 nF to 1426.00 nF. The response and recovery times were determined to be ~20 s and ~3 s, respectively. The maximum hysteresis of the sensor was evaluated to be ~4.16% occurred at 85.1% RH. The sensor was proved to be with long-term stability, with a maximum capacitance relative standard deviation of ~3.78% at 11.3% during a 50-day storage in ambient air. Our results indicate that ZnO/Si-NPA might be a promising candidate material for fabricating room-temperature humidity sensors.



## 1. Introduction

Humidity sensors have been widely used in the field of industrial process control, environment monitoring, and agricultural or medical detection and analysis [1–3]. In the past decade, there has been increasing interest in developing high performance humidity sensors based on metal oxides [4,5], polymers [6] and inorganic/organic composite materials [7,8], and the application of various nanostructures was thought to be a promising approach to promote further the device performances [9–11]. Among the widely studied nanostructured sensing materials, ZnO was one of the most promising candidates, because the merits of its low-cost preparation, plentiful and controllable surface morphology, high chemical and thermal stability, and high electrical sensitivity to gas adsorption made it very competitive for fabricating practical gas sensors [12,13].

In the past several years, lots of researches have been devoted to improve the device performances of gas sensors based on various ZnO nanostructures such as nanowires [14], nanorods [15], flowerlike nanostructures [16], hollow spheres [17], and porous architectures [18]. For example, ZnO nanorod was found to be highly responsive to low-concentration ethanol at an elevated temperature [19] and $H_2S$ at room temperature [20], and porous ZnO nanoplates could exhibit alternative response to chlorobenzene and ethanol at different operating temperatures [21]. Compared with the detection of various gases, the study on the humidity sensing properties of ZnO nanostructures was seldom reported. But humidity responses were also observed in the films of LiCl-doped ZnO nanofibers and ZnO nanotetrapods [22,23]. Therefore, a further investigation on the humidity sensing properties of ZnO nanostructures would be of importance for either developing high-performance humidity sensors or preparing integrated multi-functional humidity-gas co-detectors.

In the previous study, we reported the preparation and characterization of silicon nanoporous pillar array (Si-NPA), a unique silicon hierarchical structure prepared by a hydrothermal etching method [24]. Based on Si-NPA, capacitive humidity sensors with high sensitivity, short response and recovery times were obtained, and the good performance was attributed to the formation of the regularly arrayed and highly nanoporous silicon pillars [25]. However, Si-NPA was easily oxidized in air due to its high surface chemical activity [24], which would unavoidably damage the stability of the humidity sensors made of Si-NPA. To promote the stability, humidity sensors based on multi-wall carbon nanotubes (MWCNTs), magnetite nanocrystallites (*nc*-$Fe_3O_4$), and silicon carbide nanowires (*nw*-SiC)/Si-NPA were prepared [26–28]. Although

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the device stability was greatly improved through encapsulating Si-NPA with these functional nanomaterials and much higher sensitivity was obtained, the response and recovery times were prolonged by-productively [26–28]. For example, the response and recovery times for Si-NPA sensors were 11 s and 2 s, while those for MWCNTs/Si-NPA, *nc*-$Fe_3O_4$/Si-NPA, and *nw*-SiC/Si-NPA sensors were prolonged to ~64 min and 51 min, 20 s and 15 s, and 105 s and 85 s, respectively [26–28]. The prolonging of the response and recovery times might originate from the special surface morphology and nanostructures formed on Si-NPA, such as the entangled MWCNTs, porous *nc*-$Fe_3O_4$ thin film and entangled SiC nanowires [26–28]. Considering the plentiful morphology and easy controlling of ZnO nanostructures, the status might be improved through preparing ZnO/Si-NPA with certain distinctive surface morphology and microstructure.

In this paper, we report that a ZnO cauliflower array was prepared by growing ZnO on Si-NPA via a chemical vapor deposition (CVD) method. Considering the advantages of the wide humidity operating range and the relatively simple electronics for capacitive sensors over gravimetric, electromagnetic, and resistive sensors [29], a capacitive humidity sensor was made based on ZnO/Si-NPA. The room-temperature humidity sensing properties of ZnO/Si-NPA, including the response and sensitivity, response and recovery times, hysteresis, measurement reproducibility, and long-term stability, were studied systematically. Our results indicated that ZnO/Si-NPA might be an ideal sensing material for fabricating practical humidity sensors.

## 2. Experimental details

As has been described in detail elsewhere [24], Si-NPA was prepared by hydrothermally etching (1 1 1) oriented, heavily boron-doped single crystal silicon (*sc*-Si) wafers in the solution of hydrofluoric acid containing ferric nitrate. All the *sc*-Si wafers were cut as rectangles specified by 15 mm × 20 mm. The chemical vapor deposition of ZnO on Si-NPA was performed in a horizontal tube furnace. Both the high-purity Zn powder, which was used as Zn source, and the Si-NPA substrate, were placed at the constant-temperature zone of the furnace, with the latter being placed 2 cm away from the Zn source downstream to the carrier gas. After the chamber inner pressure was pumped down to ~50 Pa, high-purity argon and oxygen flows were introduced, with rates of 200 sccm and 2 sccm, respectively. Then the chamber was heated up to 900 °C with a rate of 10 °C/min and then maintained at the temperature for 30 min. Finally, with a rate of 10 °C/min, the furnace was cooled down to room temperature. The chamber inner pressure during the whole CVD process was maintained at 300 Pa. The humidity sensor was prepared through magnetron sputtering coplanar interdigital silver electrodes onto ZnO/Si-NPA. Two silver wires were solidified onto the electrodes by conductive silver paste to connect the ZnO/Si-NPA sensor with the testing instrument.

The crystal structure and surface morphology of as-prepared ZnO/Si-NPA were characterized by a powder X-ray diffractometer (XRD, Panalytical X′ Pert Pro) using Cu K(1 radiation (0.15406 nm) as the X-ray source and a field-emission scanning electron microscope (FE-SEM, JSM 6700F), respectively. The capacitance response to humidity was measured using a TH2818 automatic component analyzer and an LCR multi-frequency meter at different frequencies. The humidity environments were provided by encapsulating a series of standard saturated salt solutions (LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl and $KNO_3$) in conical flasks with stoppers. At the environmental temperature of 22 °C, the corresponding relative humidity (RH) levels were ~11.3%, ~33.1%, ~54.4%, ~75.5%, ~85.1%, and ~94.6%, respectively [30]. All the humidity sensing measurements were carried out under atmospheric pressure and at 22 °C.

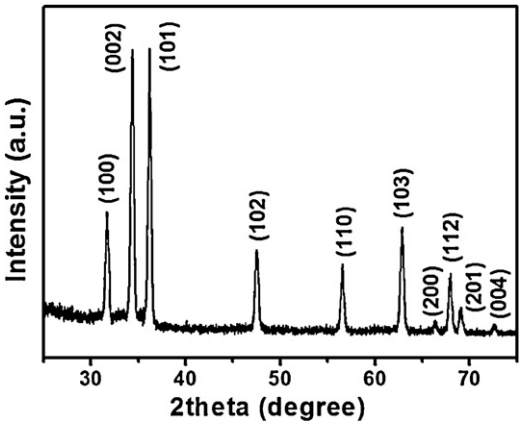


**Fig. 1.** The XRD pattern of ZnO/Si-NPA.

## 3. Results and discussion

Fig. 1 shows the XRD pattern of as-prepared ZnO/Si-NPA. Here ten diffraction peaks were observed and all of them were indexed to hexagonal wurtzite ZnO. These peaks were clear and sharp, which indicates that as-grown ZnO was of good crystallinity. As has been disclosed previously [24], Si-NPA was of a hierarchical structure characterized by its regular pillar array. Its typical surface morphology was shown in Fig. 2(a). After the CVD process, the surface morphology of ZnO/Si-NPA was presented in Fig. 2(b) and (c). From the FE-SEM image with low magnification (Fig. 2(b)), a regular array composed of well-separated ZnO cauliflowers was observed, although the valleys surrounded the cauliflowers were also covered with a continuous thin film of ZnO nanoparticles. Judged from the FE-SEM image with high magnification (Fig. 2(c)), it was found that each cauliflower was composed of plenty of small protrusions, just like undeveloped flower buds. The average size of the cauliflower head was ~3 μm in diameter. All these flower buds grew perpendicularly to the local surface of the cauliflower head, with a size range of ~180–350 nm and an average height of ~300 nm. Clearly, the regular array as well as the hierarchical features of ZnO cauliflowers could provide an effective path for gas transport and an enlarged specific area for gas sensing, and both of which might brought enhanced humidity sensing effects. Furthermore, because the surface of Si-NPA, both the pillars and the valleys around the pillars, were well covered by ZnO and an obvious rectifying behavior could be observed in the *I–V* curve of ZnO/Si-NPA (not shown), the humidity sensing properties of ZnO/Si-NPA should mainly come from the deposited ZnO material.

The device response strongly depends upon the testing frequencies for capacitance sensors. To find the suitable testing frequency, we measured the RH capacitance response under four frequencies, 100 Hz, 1 kHz, 5 kHz and 10 kHz, respectively. The capacitance-RH curves measured at the four frequencies were depicted in Fig. 3(a). The fact that the capacitances measured under all the four frequencies increased monotonically with RH suggested that ZnO/Si-NPA might be a suitable material for humidity detection. With the RH changed from 11.3% to 94.6%, the capacitance measured under the four testing frequencies increased from 20.1, 6.62, 4.93, and 3.29 to 2920.00, 1426.00, 922.32, and 517.63 nF, respectively, with the capacitance increments being ~14,430%, 21,440%, 18,610%, and 15,630% correspondingly. The maximum signal increment was achieved under 1 kHz. Compared with the maximum signal increment achieved by Si-NPA, MWCNTs/Si-NPA, *nc*-$Fe_3O_4$/Si-NPA, and *nw*-SiC/Si-NPA [25–28], which were ~2048% (capacitance, at 100 Hz), 362% (resistance), 12,000% (capacitance, at 1 kHz), and 966% (capacitance, at 100 Hz), respectively, such an increment was much higher. It was generally accepted that the