proceedings

Eurosensors PARIS 2017 September 3-6 • 2017 • XXXI conference

MDPI

Proceedings

Fabrication of ZnO Nanorods on MEMS Piezoresistive Silicon Microcantilevers for Environmental Monitoring †

Jiushuai Xu [1,2,*], Maik Bertke [1,2], Alaaeldin Gad [1,2,3], Feng Yu [1,2], Gerry Hamdana [1,2], Andrey Bakin [1,2] and Erwin Peiner [1,2]

[1] TU Braunschweig, Department of Semiconductor Technology, Braunschweig, Germany; M.Bertke@tu-bs.de (M.B.); agadnrc@gmail.com (A.G.); f.Yu@tu-bs.de (F.Y.); g.hamdana@tu-bs.de (G.H.); a.bakin@tu-bs.de (A.B.); E.Peiner@tu-bs.de (E.P.)

[2] Laboratory for Emerging Nanometrology (LENA), Braunschweig, Germany

[3] Inorganic Chemistry Department, National Research Centre (NRC), Cairo, Egypt

* Correspondence: jiushuai.xu@tu-bs.de; Tel.: +49-531-391-3806

† Presented at the Eurosensors 2017 Conference, Paris, France, 3–6 September 2017.

Published: 16 August 2017

Abstract: In this study, a ZnO nanorods (NRs) patterned MEMS piezoresistive silicon micro-cantilever was fabricated as environmental monitor. The fabrication starts from bulk silicon, utilizing photolithography, diffusion, inductively coupled plasma (ICP) cryogenic dry etching, Zinc DC-sputtering, and chemical bath deposition (CBD) etc. This sensor shows a humidity sensitivity value of 6.35 ± 0.27 ppm/RH% at 25 °C in the range from 30% RH to 80% RH.

Keywords: MEMS; Micro-cantilever; ZnO nanorods; seed layer; environmental sensor

1. Introduction

ZnO nanomaterials, especially the ZnO 1D nanostructures such as nanowires, nanorods, nanopowders, and nanotubes have been recently attracting interest for the detection of humidity, chemicals and gases due to their large surface-to-volume ratio, high density of surface vacancies and chemisorption active sites [1,2]. Their low-cost facile fabrication process, good stability (due to the high crystallinity) and integration capabilities make it possible to fabricate ZnO nanostructure [3] on micro-cantilevers. Furthermore, with ZnO nanostructure-coated micro-cantilevers mass changes induced by deposited gas molecules of ppm concentrations can be detected [4]. The resonant frequency (f) shifts can be directly read out, thus they are suitable for pocketsize environmental monitoring devices [5].

2. Experimental

2.1. Fabrication of ZnO NRs Patterned Self-Resonant Micro-Cantilever

Figure 1 depicts the fabrication process steps of the ZnO NRs patterned MEMS piezoresistive micro-cantilever environmental sensor, and the details are described as follows:

(a) The fabrication started from a piece of sample with a dimension of 30 × 30 mm² cut from an *n*-type bulk-silicon wafer (crystal orientation: <100>; resistivity: 1–10 Ω·cm; thickness: 275 ± 15 μm and diameter: 100 ± 0.13 mm). Comparing to silicon-on-insulator (SOI) wafers, the bulk silicon is preferred because of its lower price, high mechanical quality factor and larger flexibility for geometrical resonant micro-cantilever designing.

(b) A 300 nm thick SiO_2 layer was subsequently grown during a thermal oxidation process. The oxidation step was carried out by putting the sample into a furnace with a constant temperature of 1100 °C. This oxide layer was grown and used as a mask for subsequent n^+-, p- and p^+-diffusions.

(c) After that, a positive photoresist (AZ 5214E, Shipley) was utilized during the photolithography step and a MJB4 mask aligner (SÜSS MicroTec AG, Garching, Germany) was used to expose the pattern area. Prior to the exposure, the photoresist spin-coating procedure was run at a speed of 5000 rpm for 35 s, to create a homogenous photoresist layer of 1.5 μm in thickness. After the exposure, the sample was then dipped and developed in AZ 726 MIF developer solution (Rohm and Haas, PA, USA) for 60 s, followed by DI water rinsing and nitrogen purging. Subsequently, the sample was dipped into buffered hydrofluoric acid solution (HF, 6–7%) for 12 min to remove the oxide layer and produce the pattern area for the phosphorus spin-on emulsion coating (3000 rpm, 30 s). Finally, the n+ diffusion was performed by putting the sample into a furnace with a temperature of 1100 °C for 30 min.

(d) Afterwards, patterned areas for creating the electrical structure elements of sensor (the Wheatstone bridge, the heating resistor and sampling electrode) were fabricated by a similar procedure as described in c): thermal oxidation, spin-coating, photolithography and etching. The electrical structure element on the sample were produced by spinning-on Borofilm 100 emulsion (Emulsitone Company, NJ, USA) and the following diffusion at 1100 °C for 30 min.

(e) An additional boron diffusion step was performed to reduce the contact resistance between the p-doped silicon zone and the metal (i.e., ohmic contact). The p^+-diffusion was implemented exactly to the square areas where the metal contact zone will be deposited.

(f) Then a polycrystalline Zn film was prepared by sputtering Zn (99.99%) using high purity Ar (99.99%) gas under 50 μA direct current (DC). The sputtered Zn film was oxidized through annealing in air at 300 °C for 60 min to obtain a crystalline ZnO seed layer. The thickness of the seed layer was controlled by adjusting the sputtering time, which is 40 min in our fabrication process, and the seed layer sputtering was only applied to the micro-cantilever area.

(g) After the DC-sputtering, a bilayer of 30 nm thick chromium (Cr) and 300 nm thick gold (Au) were deposited as the metallization by electron-beam physical vapor deposition, the chromium layer serves to improve the adhesion of gold and silicon.

(h) To create the micro-cantilever, the front-side sample-shaping step was executed utilizing a SI 500C cryogenic dry etcher (SENTECH Instruments, Germany), the etching procedure was carried out for 15 min to produce micro-cantilevers with a thickness of 15 μm. During etching the ZnO crystalline seed layer was protected by photoresist coating.

(i) Chemical bath deposition (CBD) for ZnO NRs was performed on top of the crystalline ZnO seed layer, the sample was put into the CBD solution consisting of 25 mmol/L zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 25 mmol/L hexamethyleneteramine (HMT, $C_6H_{12}N_4$,) for 3 h at 90 °C in a temperature controlled chemical reactor.

(j) In the last step, the backside etching was executed to finally release the micro-cantilever. The process was carried out using the same recipe as for front-side etching with photoresist serving as the protecting mask.

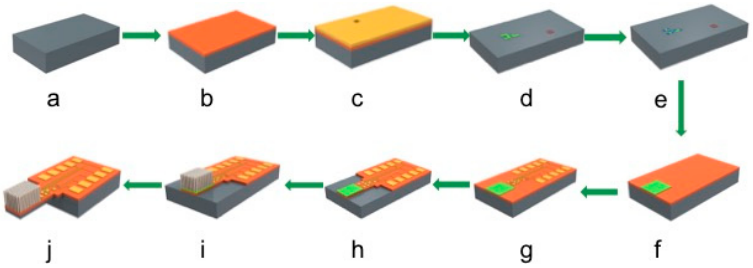

Figure 1. Schematic of fabrication of ZnO-NRS-patterned piezoresistive Si-micro-cantilever environmental sensor.

2.2. Characterization

The morphology of the grown ZnO NRs was characterized using scanning electron microscopy (SEM). The silicon cantilever was operated in resonance by driving a signal composed of DC (5 V) and AC (2.5 V) voltage through a *p*-doped heating resistor, across which the electric current is dissipated, thus generating a periodic Joule heating effect and therefore actuate the cantilever to vibrate. A multimeter and a spectrum analyzer were used to record and analyze the reading of a piezoresistive Wheatstone bridge, which was operated at a voltage of 1 V from a DC power supply (HP 34401 A). Furthermore, the resonant frequency shifts of the fabricated ZnO NRs patterned piezoresistive micro-cantilever sensor under different relative humidity and temperature were measured in a climatic chamber (Weiss SB22/160/40; www. Bomatec.ch).

3. Results and Discussion

High surface area and fast electron transfer along their axial direction of ZnO are vital parameters for their brilliant sensing performance [1]. The seed layer, which can reduce the lattice mismatch between ZnO nanostructures and the silicon substrate, therefore leading to a well-aligned growth of ZnO nanostructures on silicon, plays a crucial role in ZnO growing.

Figure 2 shows the representative SEM views of ZnO NRs deposited directly on the bulk silicon cantilever (left) and ZnO NRs grown on the cantilever with a CBD (zinc acetate dihydrate (Zn(Ac)2·2H2O), sodium hydrate (NaOH), and methanol) seed layer (right). The difference between two areas is obvious. The ZnO NRs formed directly on the cantilever are randomly distributed in all directions relative to the cantilever surface, while ZnO CBD growth on a CBD seed layer lead to a homogeneous, aligned array of ZnO NRs. Figure 3 depicts a schematic and SEM views of a MEMS piezoresistive micro-cantilever with a DC-sputtered ZnO seed layer. It is clearly seen, that ZnO NRs grown on a sputter-coated seed layer have a preferred deposition orientation in the <001> direction perpendicular to the cantilever top surface. In addition, the parameters of different NRs were compared in the Table 1, giving evidence that the ZnO NRs deposited on sputter-coated seedlayers are preferred for sensing applications in combination with micro cantilevers due to their high surface-to-volume ratio, better alignment, controllable surface morphology and area density.

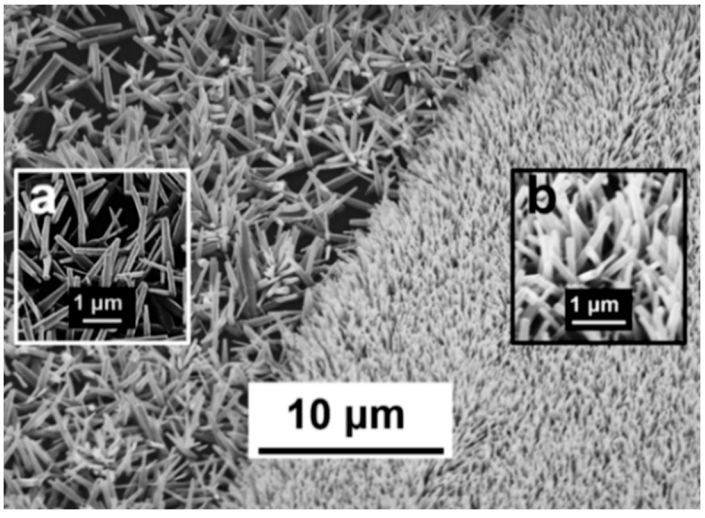

Figure 2. SEM of ZnO NRs directly on the cantilever (left) and on CBD seed layer (right), insets are their corresponding magnified views.

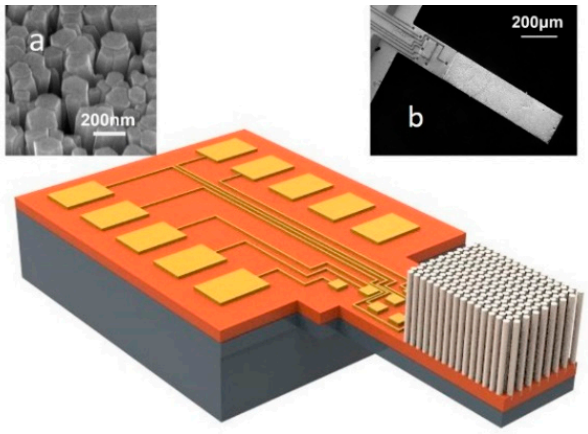

Figure 3. ZnO-NRs-patterned piezoresistive Si microcantilever sensor, (**a**) SEM of ZnO NRs on a sputtered seed layer; (**b**) SEM of microcantilever with ZnO NR array.

Table 1. Parameters of ZnO NRs on different types of seed layers.

Seedlayer Type	Diameter/nm	Length/nm	Area Density/μm^{-2}
Without seedlayer	195 ± 45	2203 ± 225	2.7 ± 0.8
CBD seedlayer	115 ± 26	995 ± 98	26 ± 1
Sputter coating seedlayer	144 ± 24	1348 ± 39	38 ± 2

The ZnO-covered cantilevers were then operated in a temperature- and humidity-controlled climatic chamber for the investigation of humidity sensing. Fano-resonance based model fitting [6] results indicated that multi-layer ZnO-NRs-patterned piezoresistive micro-cantilevers sensor have a sensitivity value of 6.35 ± 0.27 ppm/RH% at 25 °C in the range from 30% RH to 80% RH (Figure 4). This sensitivity is higher than 0.05 ppm/RH% and 0.12 ppm/% reported for sol-gel ZnO nanowires and nanoparticles, respectively, on a quartz crystal balance [7] and ZnO quantum dots on a QCM with 5–10 ppm/% [8]. Besides, to improve the sensitivity, a new type 3D columnar cacti- like ZnO NRs @ Si NRs (Figure 5) based on Atomic layer deposited seed layer has been fabricated on the micro-cantilever, which is supposed to have much larger surface-to-volume ratio, higher density of surface vacancies and more chemisorption active sites required for gas sensing. Therefore, the sensor presented here is a very promising candidate for humidity sensing applications.

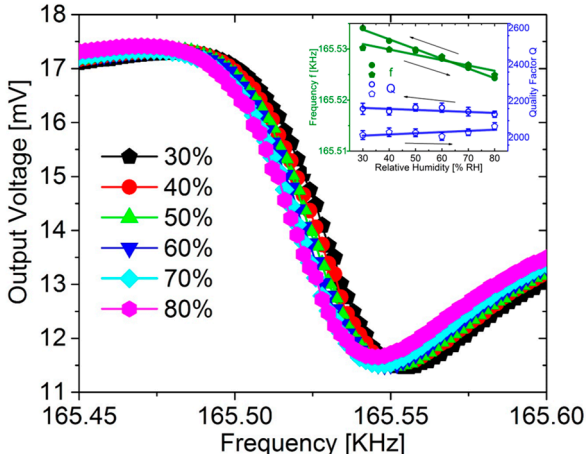

Figure 4. Resonant frequency under different humidity level, inset f and Q-factor vs. relative humidity.

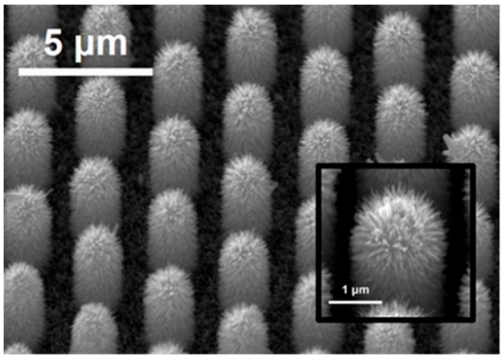

Figure 5. SEM of 3D columnar cacti-like ZnO NRs @ Si NRs and its magnified view (inset).

4. Conclusions

A MEMS piezoresistive silicon micro-cantilever environmental sensor was fabricated from a bulk silicon. This gravimetric sensor with ZnO NRs based on DC-sputtering seed layer as sensing material has a high sensitivity value of 6.35 ± 0.27 ppm/RH% at 25 °C in the range from 30% RH to 80% RH. In addition, by growing multi-ZnO NRs-film or 3 D NRs, a much higher sensitivity can be expected. Thus, indicating this sensor to be a potential candidate for environmental monitoring.

Acknowledgments: The authors thank Angelika Schmidt and Kerstin Franke for their valuable technical support. Xu, J. is grateful to the China Scholarship Council (CSC) for funding by a scholarship under the Grant CSC No. 201506300019. Bertke, M. and Hamdana, G. are grateful for funding by the Ministry of Science and Culture of Lower Saxony (MWK), Germany in the QUANOMET project and by the German Research Foundation (DFG) under no. PE 885/3-1, respectively.

Conflicts of Interest: The authors declare no conflict of interest.

Reference

1. Zhu, D.; Fu, Y.; Zang, W.; Zhao, Y.; Xing, L.; Xue, X. Piezo/Active Humidity Sensing of CeO_2/ZnO and SnO_2/ZnO Nanoarray Nanogenerators with High Response and Large Detecting Range. *Sens. Actuators B Chem*. **2014**, *205*, 12–19.
2. Wagner, A.; Bakin, A.; Otto, T.; Zimmermann, M.; Jahn, B.; Waag, A. Fabrication and Characterization of Nanoporous ZnO Layers for Sensing Applications. *Thin Solid Films* **2012**, 520, 4662–4665.
3. Bakin, A.; Behrends, A.; Wagner, A.; Waag, A. Zinc Oxide Nanostructures, in *Fabrication of ZnO Nanostructures*; Pan Stanford Publishing Pte Ltd.: Singapore, 2014; ISBN:978-981-4411-33-2.
4. Kilinc, N.; Cakmak, O.; Kosemen, A.; Ermek, E.; Ozturk, S. Fabrication of 1D ZnO nanostructures on MEMS cantilever for VOC sensor application. *Sens. Actuators B Chem*. **2014**, *202*, 357–364.
5. Yang, J.; Xu, J.; Wu, W.; Bertke, M.; Wasisto, H.S.; Peiner, E. Piezoresistive silicon cantilever covered by ZnO nanorods for humidity sensing. *Proc. Eng*. **2016**, *168*, 1114–1117.
6. Bertke, M.; Hamdana, G.; Wu, W.; Wasisto, H.S.; Uhde, E.; Peiner, E. Analysis of asymmetric resonance response of thermally excited silicon micro-cantilevers for mass-sensitive nanoparticle detection. *J. Micromech. Microeng*. **2017**, *27*, 064001.
7. Asar, N.; Erol, A.; Okur, S.; Arikan, M.C. Morphology-dependent humidity adsorption kinetics of ZnO nanostructures. *Sens. Actuators B* **2012**, *187*, 37–42.
8. Sakly, N.; Said, A.H.; Ouada, H.B. Humidity-sensing properties of ZnO QDs coated QCM: Optimization, modeling and kinetic investigations. *Mater. Sci. Semicond. Process.* **2014**, *27*, 130–139.