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Silicon Microcantilevers with ZnO Nanorods/Chitosan-SAMs Hybrids on Its Back Surface for Humidity Sensing †

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Abstract: This paper reports a piezoresistive silicon microcantilever-based gravimetric humidity sensor, where a ZnO nanofilm (200 nm) and ZnO nanorods (NRs) with different lengths (1.5 μm and 6 μm) modified with chitosan self-assembled monolayers (SAMs) are coated on the microcantilevers' back surface as the sensing material. Thanks to the new sensor design, the resonant frequency (RF) shifts induced by the mass adsorption on the high surface-area-to-volume ratio, hybrid-sensing nanostructure can be tracked directly by monitoring the output of the *p*-diffused full Wheatstone bridge. By depositing ZnO NRs and Chitosan SAMs, direct-reading microcantilevers with high repeatability, reliability and high sensitivity (15 Hz/%RH) can be achieved.

Keywords: microcantilever; ZnO nanorods; Chitosan SAMs; humidity sensing

1. Introduction

Micro and nano cantilevers have been investigated by many groups for chemical and biological sensors due to their extraordinary sensitivities in mass changes. For the moment, the sensitivity of these micromechanical devices is often limited by their small surface areas. To achieve better sensitivity, microcantilevers are coated with nanostructured materials due to their high total surfacearea-to-volume ratio [1]. Therefore, owing to their good stability, high sensitivity, great integration capability, and excellent chemical and biocompatibility, ZnO nanostructures were used for various applications, including chemical sensors, solar cells, and photodetectors etc. In our past study, we reported the fabrication of ZnO nanorods (NRs) on the upside of microcantilevers and their humidity sensing performances [2]. In this paper, to investigate the relation of ZnO NRs and humidity sensing further, a ZnO nanofilm with a thickness of 200 nm and ZnO NRs of 1.5 μm and 6 μm in length were selectively deposited on the cantilevers' back surface as sensing material. The newly developed fabrication method was based on our reported work [2,3]. Furthermore, ZnO NRs of different lengths were additionally coated with chitosan self-assembled monolayers (SAMs). Using this hybrid nanostructure, sensitivity was substantially improved.

2. Experimental

2.1. Microcantilever Fabrication

A schematic graph of a Si microcantilever with ZnO NRs on its back surface is shown in Figure 1. Considering their low price, high mechanical quality factor, high stability, and high degree of freedom for geometrical resonant cantilever design, *n*-type bulk silicon was used as the fabrication substrate. With the help of photolithography, n_+-diffusion, *p*-diffusion and p_+-diffusion were successively completed on the patterned area by doping phosphorus and boron, respectively, to create a substrate contact, a heating resistor for actuating in-plane cantilever bending, and a full Wheatstone bridge for reading out. Besides, a bilayer of 300 Å thick chromium and 3000 Å gold was deposited by e-beam physical vapor deposition as the metal pad for connection. After that, a microcantilever with a dimension of 1000 μm in length, 170 μm in width and 50 ± 10 μm in thickness was obtained by back- and up-side etching using inductive-coupled plasma (ICP) cryogenic dry etching. Prior to the front-side etching, ZnO NRs were selectively and solely grown on microcantilever back surface using chemical bath deposition (CBD) on a DC-sputtered/annealed seed-layer [2]. Finally, chitosan SAMs on the ZnO NRs were deposited by dipping the cantilever into a 1% chitosan solution for 5 s. The chitosan solution was prepared by dissolving chitosan powder into 4% acetic solution and magnetic stirring for 24 h. For further details, we refer to [2,4].

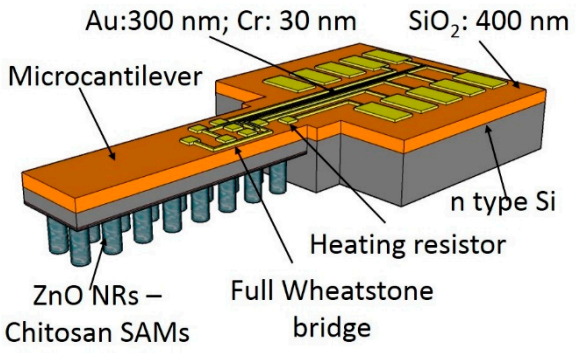

Figure 1. Schematic graph of a Si microcantilever with its back surface patterned with ZnO NRs/chitosan SAMs.

2.2. Measurement Set-Up

The microcantilevers were actuated by applying an AC voltage superimposed on a DC voltage to the heating resistor located at the cantilever clamped-end (Figure 1). Adsorption or desorption of water molecules on the microcantilever induces a proportional mass change, which then leads to a corresponding resonant frequency shift. The resonant frequency shifts can be tracked by an MFLI lock-in amplifier + phase-locked loop (PLL) system (Zurich Instrument) which was connected to the microcantilevers for on-line measurements.

3. Results and Discussion

3.1. ZnO Nanorods (NRs) Characterization

Figure 2a shows the inclined-view of a scanning electron microscopy (SEM) graph of a Si microcantilever with its back surface coated with ZnO NRs, an enlarged cross-sectional view is shown in Figure 2b. As can be observed, ZnO NRs about 6 μm in length were selectively deposited on the cantilever's back surface. The ZnO NRs were vertically oriented with respect to the substrate.

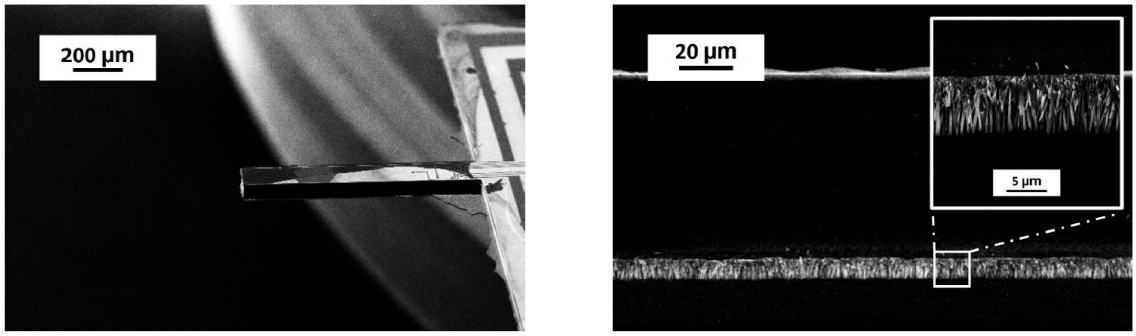

Figure 2. (**a**) Inclined-view SEM graph of Si microcantilever with its back surface coated with ZnO NRs; (**b**) and an enlarged detail in a cross-sectional view (inset shows ZnO NRs in a further enlarged view).

X-ray diffraction (XRD) was further used to characterized the crystallinity of the grown ZnO NRs arrays (Figure 3), the indexed diffraction peak is consistent with the standard value of bulk wurtzite ZnO (JCPDS 36-1451). The sharp and strong (002) peak indicates a c-axis orientation of the ZnO NRs, which is corresponding to the SEM observation in Figure 2.

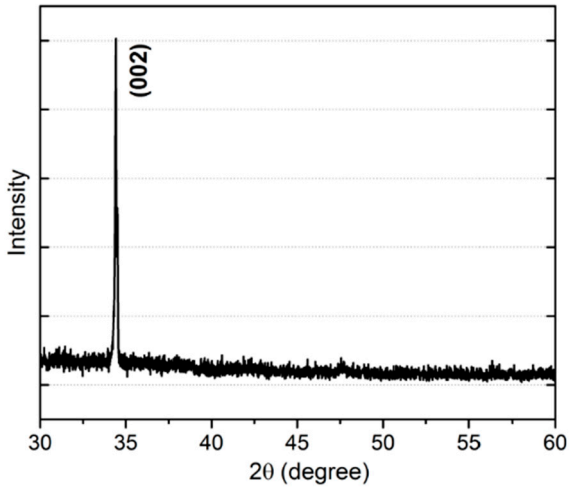

Figure 3. XRD spectra of ZnO NRs grown on a sputtered/annealed (300 °C) seed-layer.

3.2. Sensing Performance

The fabricated microcantilevers were measured for relative humidity (RH) levels ranging from 30%RH to 70%RH at 25 °C in a RH- and temperature-controlled climate chamber. 30 min was given to adjust each RH level, thus the RH in the chamber and sensing microcantilevers are assumed to reach the equilibrium. Figure 4 depicts the stability measurements of a microcantilever coated with a sputtered/annealed ZnO film (200 nm)/chitosan SAMs. We find a resonant frequency (RF) uncertainty of 0.46 ± 0.21 Hz, which may be caused by RH/temperature fluctuations in the chamber, indicating a good repeatability of the microcantilevers and a good reliability of the measurements results.

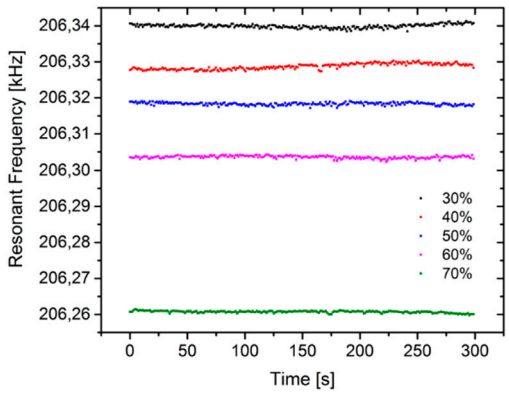

Figure 4. Short time stability of microcantilevers coated with sputtered/annealed ZnO film (200 nm)/chitosan SAMs measured from 30%RH to 70%RH at 25 °C.

A blank microcantilever and microcantilevers with a sputtered/annealed ZnO nanofilm (200 nm), ZnO nanofilm (200 nm) and additionally covered with chitosan (ZnO nanofilm/chitosan), ZnO NRs (1.5 μm), ZnO NRs (1.5 μm)/chitosan, ZnO NRs (6 μm), ZnO NRs (6 μm)/chitosan under different RH levels ranging from 30% RH to 70% RH at 25 °C, respectively, with steps of 5%RH, the measurements are performed and depicted in Figure 5. As we can see from the figure, microcantilever without sensing materials has almost no response to the RH changes, only around 0.7 Hz total RF shift was found. By depositing ZnO NRs on the microcantilever, the humidity sensing was obviously improved, and compared with microcantilever with short NRs, the microcantilever with arrays of higher surface-to-volume ratio NRs (6 μm) was proved to be have much higher sensitivity. Besides, with the modification of chitosan SAMs, a 15 times higher sensitivity can be expected, a microcantilever with ZnO NRs (6 μm)/chitosan shows a RH sensitivity of around 15 Hz/%RH.

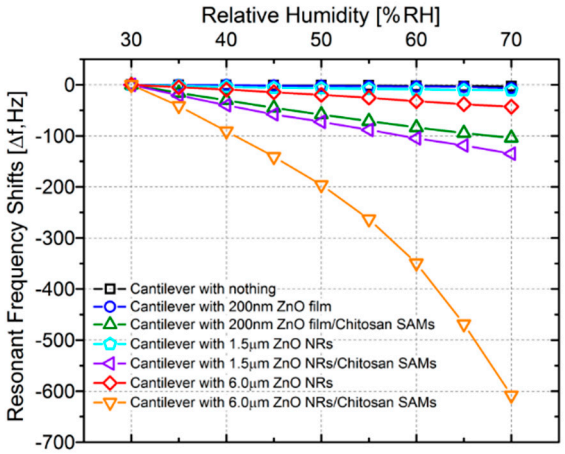

Figure 5. RF shifts of blank microcantilevers and microcantilevers with sputtered/annealed ZnO film (200 nm), ZnO film (200 nm)/chitosan, ZnO NRs (1.5 μm), ZnO NRs (1.5 μm)/chitosan, ZnO NRs (6 μm), ZnO NRs (6 μm)/chitosan under different RH levels ranging from 30% RH to 70% RH at 25 °C.

4. Conclusions

In this work, we reported the fabrication and humidity sensing of microcantilever with ZnO NRs and ZnO NRs/chitosan SAMs. Vertically oriented ZnO NRs can be selectively and solely deposited on the back surface of the microcantilever. The microcantilevers with ZnO NRs/chitosan SAMs were proved to be high sensitive to the RH changes, and the sensing performance were found to be very good repeatability and reliability, indicating that microcantilevers can be potentially used as environmental sensors, e.g., humidity sensor and gas sensor.

Author Contributions: J.X. and E.P. conceived and designed the experiments; J.X. and A.S. performed the experiments; J.X., M.F. and M.B. designed the measurement set-up, J.X., A.S. and X.L. measured and analyzed the data; E.P. contributed reagents/materials/analysis tools; J.X. wrote the paper, E.P. revised the paper, E.P. supervised the research.

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

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