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Capacitive humidity sensing behavior of ordered Ni/Si microchannel plate nanocomposites

Fengjuan Miao[a,b], Bairui Tao[a,b], Li Sun[b], Tao Liu[b], Jinchuan You[b], Lianwei Wang[b,*], Paul K. Chu[c]

[a] College of Communications and Electronics Engineering, Qiqihar University, 42 Wenhua Street, Qiqihar Heilongjiang 161006, China
[b] Laboratory of Polar Materials and Devices, Ministry of Education, and Department of Electronic Engineering, East China Normal University, 500 Dongchuan Road, Minhang District, Shanghai 200241, People's Republic of China
[c] Department of Physics and Material Sciences, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

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ABSTRACT

The preparation and humidity sensing of nickel coated silicon microchannel plate (Ni/Si-MCP) materials are studied. The silicon MCP fabricated by electrochemical etching has ordered channels and macro-porous structures. Nickel is coated by electroless plating onto the inner wall of the silicon MCP for the detection of humidity. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) are used to determine the structural and morphological properties. Our results show that the Ni/Si-MCP nanocomposites have high sensitivity and fast response time. They are compatible with current IC processes and have promising applications as integrated micro humidity sensors.

1. Introduction

Accurate and reliable measurement of water vapor is important and humidity measurement is crucial to many environmental, industrial and other applications. In order to achieve enhanced performance, some novel humidity sensors comprising nanoscale sensing elements have been developed such as nanocomposites [1–3], metal oxide nanocrystals [4–6], nanowires [7–9], nanorods [10,11], nanotubes [12], porous inorganic/organic materials and so on [13]. Although these nanoscale materials make particularly appealing in the humidity detection due to their large surface-to-volume ratio, some technique problems of compatibility with the traditional IC processing restrict their application.

Porous materials are especially attractive in sensing applications due to their large specific surface area. In particular, porous silicon (PS) has excellent mechanical and thermal properties and is compatible with silicon-based microelectronics technology [14,15]. Hence, now the jobs are partly focused on the development of PS humidity sensor [13–16]. Normally the sensor developed from PS need extra heating equipment and has long response time, and it is not suitable for whole humidity range since the hydrophobic surface [17–20]. Therefore, it is a significant challenge to establish a porous silicon-based humidity sensor with new nanostructures and modified surface [21].

In this paper, nickel/silicon microchannel plate (Ni/Si-MCP) composites were prepared and developed to a novel humidity sensor. First, the Si-MCPs were fabricated by electrochemical etching, which are macro-porous of ~5 μm width and channel ordered materials of ~200 μm height. Then, Ni/Si-MCP composite structures were obtained by the electroless plating nickel onto the surface of Si-MCP. Next, the Ni/Si-MCP composites were employed as the sensing material to develop the humidity sensor. Finally, the sensing characteristics and performance of the sensor have been investigated by detection the capacitance variations of Ni/Si-MCP composite corresponding to the water vapor adsorption/desorption.

2. Experimental details

2.1. Fabrication of large surface area Si-MCP

The starting substrate was a 525 μm p-type ⟨1 0 0⟩ silicon wafer with a resistivity of 8–12 Ω cm. The silicon MCP structure was fabricated by electrochemical etching in a mixture of hydrofluoric acid and dimethylformamide (DMF) with an appropriate amount of HCl (HF concentration of 2 M and pH value near 3). The applied voltage was controlled in the range of 0–24 V to keep the current density constant by a feedback-loop circuit. A 120 W tungsten-halogen lamp was utilized to illuminate the wafer as auxiliary

* Corresponding author. Tel.: +86 21 54345160; fax: +86 21 54345119.
E-mail address: lwwang@ee.ecnu.edu.cn (L. Wang).

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Table 1
Materials and conditions used in the electroless plating nickel process.

Chemicals	Concentration (M)	Main functions
$NiSO_4 \cdot 6H_2O$	1	Ni source
$(NH_4)_2SO_4$	1	Buffering agent
Sodium dodecyl sulfate	0.1	Stabilizing agent
NH_4F	7.5	Reductant
Sodium citrate	0.3	Complexing agent
Ammonia	X	Adjust pH 8.0–8.5

excitation. The detailed electrochemical process can be found elsewhere [22,23].

2.2. Fabrication of ordered Ni/Si-MCP composites

Electroless plating was employed in our experiments because the channels in the Si-MCP could be coated with nickel metal uniformly and the thickness of the metal film could be easily controlled via the bath composition and temperature [24]. Before electroless plating, the silicon wafer was cut into rectangular chips with dimensions of about 1 cm × 1 cm. The sample was annealed to enhance the stability of the structure. The sample surface was activated by immersing in a buffer solution (Triton X-100) before introducing into the plating bath. This way could be instead of conventional method of modifying a certain amount of Pd nuclei [25]. Electroless plating of nickel was carried in a plating bath and the materials and conditions are summarized in Table 1. The detailed roles of each ingredient can be found elsewhere [26,27]. In practice, the plating bath temperature was kept at 84 °C while continuously stirred and the pH was maintained at 8–9. After 6 min, the samples were taken out, cleaned with deionized water, and dried at 30 °C by nitrogen to produce the Ni/Si-MCP nanocomposites. In order to investigate the influence of annealing the Ni/Si-MCP was annealed at 600 °C for 360 s under argon after plating [28].

2.3. System of humidity sensing detection

First, a screen printed interdigitated electrode was fabricated on the surface of Ni/Si-MCPs by silver past, where the electrode width was 0.5 mm and the electrode distance was 1 mm. Next, two copper leading wires were glued onto the interdigitated electrode. At last, the humidity prototype sensor was constructed by fixing the Ni/Si-MCPs chip on an ~1 cm^2 PCB (printed circuit broad) by glass cement. The equivalent circuit model of the humidity sensors is illustrated in Fig. 1. It is reasonable to presume that the connection between the two adjacent Si-MCPs can be simplified into a parallel circuit cell. Each cell can be simplified into the parallel connection of a resistors R_p, and capacitors C_i. The resistor R_p represents the influence of silicon itself. The capacitors C_i represent the capacitances between two adjacent charge individual channels. The sensor prototype is equivalent to the sum of lots of cells in serial and parallel. The total capacitance C can be equivalent to the sum of lots of capacitors in serial and parallel connection. We use the resistor R_s to represents the influence of all the loss in circuit.

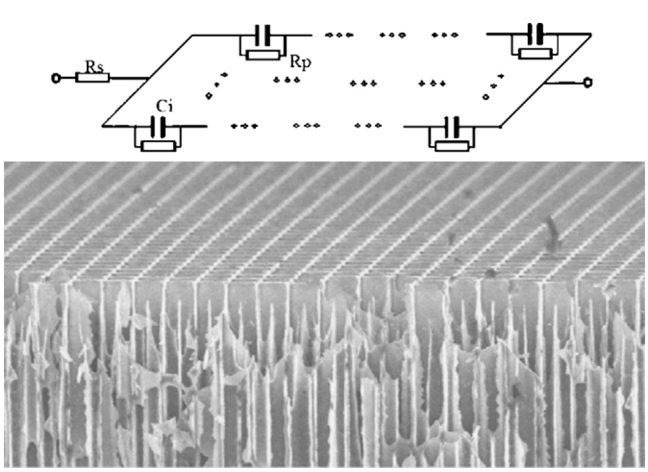

Fig. 1. Equivalent circuit model of the humidity sensor.

The resistance and capacitance are affected by the humidity in the vicinity. According to the expression of capacitance, $C = \varepsilon_0 \varepsilon (A/d)$, where C is the capacitance between two adjacent channels, ε_0 is the vacuum dielectric constant, ε is the dielectric constant of a material between each channel, A is the effective overlap area between two channels, and d is the effective distance between two channels, water vapor adsorption onto the MCP can cause the variation of ε giving rise to changes in the capacitance. Furthermore, according to the resistance formula, $R = \rho(L/S)$, where R is the equivalent resistance of the materials between two adjacent channels, ρ is the resistivity of the material, L is the effective distance between two adjacent channels, and S is the effective contact area between two adjacent channels, it is can be deduced that the resistance is hardly affected by water vapor adsorption onto the MCP.

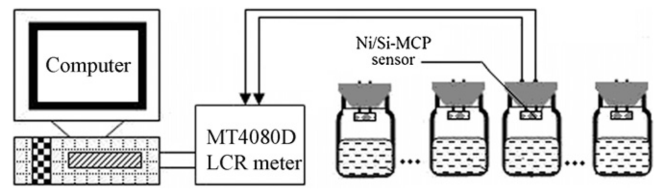

Fig. 2. Schematic diagram of the testing platform of the Ni/Si-MCP based humidity sensor.

Fig. 2 illustrates the schematic diagram of the testing platform of the humidity sensors. The relative humidity (RH%) level was controlled by saturated aqueous solutions of LiCl, CH_3COOK, K_2CO_3, NaBr, NaCl, KCl, K_2SO_4 in a closed glass vessel at an ambient temperature of 25 °C. The RH% is approximately 11.3%, 22.5%, 43.2%, 57.6%, 75.3%, 84.4%, 97.3%, respectively. The MT4080D Meter connected with a computer was used to measure the changes in the sensor capacitance in real time.

3. Results and discussion

3.1. Characterizations of sensing materials

The SEM image of the silicon MCP fabricated by electrochemical etching is depicted in Fig. 3. The surface has a regular square morphology with all the channels being aligned orderly. The width of each hole is about 5 μm and the etched depth reaches approximately 200 μm. There are little impurities in each channel, and both the length and width of the silicon Si-MCP can be varied by altering the etching time, etchant, and temperature. The Si-MCP can be lifted off from the silicon substrate and so the sensing materials are in the form of a connective film.

All above results imply that the Si-MCPs are microporous and channel ordered materials, which may have better humidity response than other porous materials due to the good fluidity for water vapor.

The MCP sidewalls are coated with Ni from reduction of metal ions in the solution. NH_4F plays an important role in the plating process. The major chemical reaction is $Si + 6F^- + 2Ni^{2+} \rightarrow SiF_6^{2-} + 2Ni$ [29,30]. The SEM images acquired from the Ni/Si-MCP composite sample without annealing are depicted in Fig. 4. The nickel particles are uniform distribution on the sidewalls of the Si-MCP. The EDS