FACILE FABRICATION OF HETEROGENEOUS NANOMATERIAL ARRAY TOWARDS LOW-POWER AND MULTIPLEXED GAS SENSING APPLICATION

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ABSTRACT

We fabricated heterogeneous metal oxide nanomaterial array consisting of CuO nanospikes, ZnO nanowires, and TiO_2 nanotubes for multiplexed gas sensing. We developed selective synthesis and integration method for various nanomaterials in a small area by using a sequential combination of localized hydrothermal and liquid phase deposition methods. This method is low-cost and eco-friendly process because of its low reaction temperature, minimal usage of liquid precursor, and localized synthesis. The device shows good mechanical and electrical connection for gas sensing. The device is expected to be applicable for multiplexed gas sensing because of its high sensitivity by using nanomaterials, outstanding selectivity by using heterogeneous material array and low-power consumption by using small and highly integrated sensing materials.

KEYWORDS

Sensor array, Metal oxide nanostructure, Localized synthesis, Multiplexed sensor

INTRODUCTION

Recently, the metal oxide nanomaterial sensors have been widely researched and shown outstanding sensing performances due to their high sensitivity and fast response caused by large surface-to-volume ratio and chemical reactivity [1]. However, controllable and reliable synthesis and integration of nanomaterials on electronic devices is still very challenging. Nanomaterials are usually synthesized in powder form or on silicon wafer by thermal evaporation, vapor-phase transport, metal-organic chemical vapor deposition, sol-gel and hydrothermal method. These methods require additional separation, dispersion and re-assembly processes for the device fabrication. Many methods have been developed for the integration of nanostructures, including random dispersion, dielectrophoresis and microcontact printing. However, these methods cannot secure reliable, controllable and repeatable integration and require expensive setups. Furthermore, these methods are adequate for the integration of the only single type nanomaterials.

In order to realize multiplexed gas sensors with high accuracy and low power consumption, we suggest a sensing device structure integrated with multiple types of heterogeneous nanomaterials. CuO nanospikes, ZnO nanowires, and TiO_2 nanotubes are well known for their excellent gas sensing properties [2]. In this work, these nanomaterials were integrated within microscale region on a single sensor chip by using a novel synthesis method based on sequential liquid-phase reactions. The power consumption for heating to operation temperatures of gas sensors can be reduced by minimizing heating areas and accurate estimation of each gas concentration in multiple gas mixture can be achieved by analyzed signals from an array of multiple heterogeneous sensing nanomaterials. We made metal oxide nanostructure array by combining localized hydrothermal [3, 4] and liquid phase deposition (LPD) processes [5], both of which are low-cost, low-temperature, and eco-friendly processes.

EXPERIMENT

Sensor Platform Fabrication

For synthesizing an array of three different nanomaterials in an ultra-small area, we fabricated devices with three individual microheaters by using a MEMS process. Three gold microheaters were patterned on Si wafer by evaporation and metal lift-off process. The gaps between three microheater arrays are only about 150 μm. The larger gap makes easier selective synthesis but that needs higher energy for heating during sensor working. We found appropriate gap by considering the heat transfer for both nanomaterial synthesis and sensor operation. SiO_2 film was deposited on microheater layer by plasma enhanced chemical vapor deposition (PECVD) for electrical insulation and three gold electrodes were patterned on the SiO_2 layer by aligning with the underlying microheaters (Figure. 1).

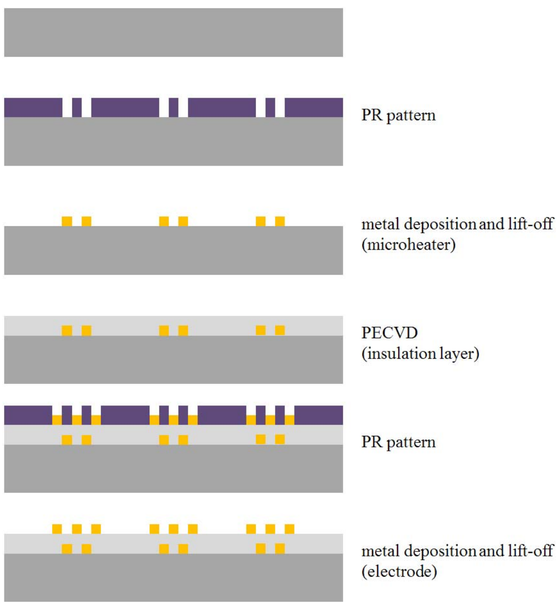

Figure 1: Diagram of the fabrication of microchip integrated with microheaters and interdigitated sensing electrodes array for multiplexed nanostructure synthesis

Nanomaterials Synthesis Process

As shown in Figure 2, the synthesis process for heterogeneous nanomaterial array consists of three steps: CuO nanospike synthesis, ZnO nanowire synthesis, conversion of ZnO nanowires to TiO_2 nanotubes, and ZnO nanowires synthesis.

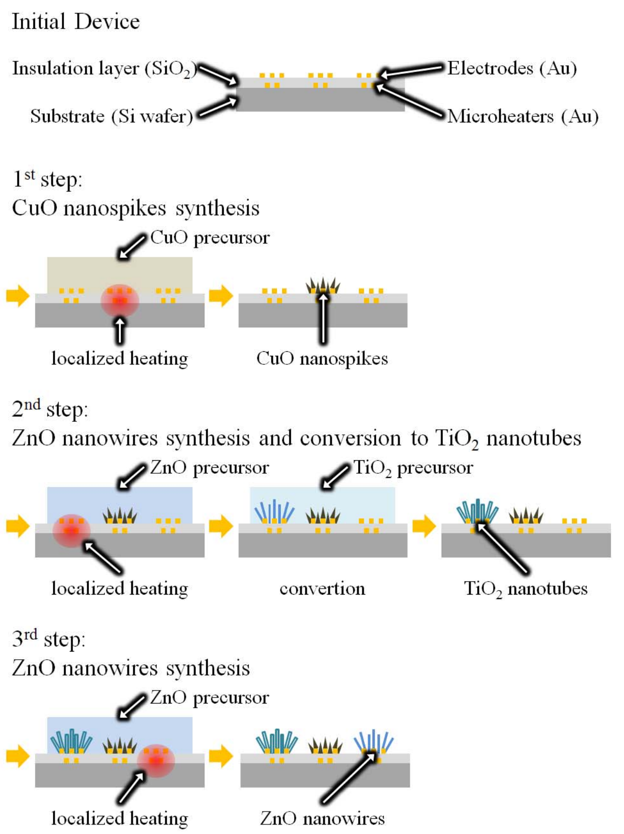

Figure 2: Schematic of the nanostructure array fabrication process: CuO nanospike synthesis, ZnO nanowire synthesis, conversion of ZnO nanowires to TiO_2 nanotubes and ZnO nanowire synthesis

In step 1, CuO nanospikes were synthesized on the electrode-II by using local Joule heating with an embedded microheater. The aqueous CuO precursor with 4 mM copper nitrate and 4 mM hexamethyltetraamine (HMTA) was used for CuO nanospike synthesis. A small PDMS block with circular well held the precursor on the electrodes and 2.2 V of electrical bias was applied to only the microheater-II. The precursor on the microheater-II was heated to a critical temperature for synthesis CuO nanospikes by Joule heating and electrode-II was connected by synthesized CuO nanospikes. We believe the following chemical reactions are involved in the synthesis of CuO nanospikes:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (2)$$

$$2OH^- + Cu^{2+} \rightarrow CuO(s) + H_2O \quad (3)$$

Although all of three electrodes were exposed to the precursor, CuO nanospikes were synthesized on only electrode-II.

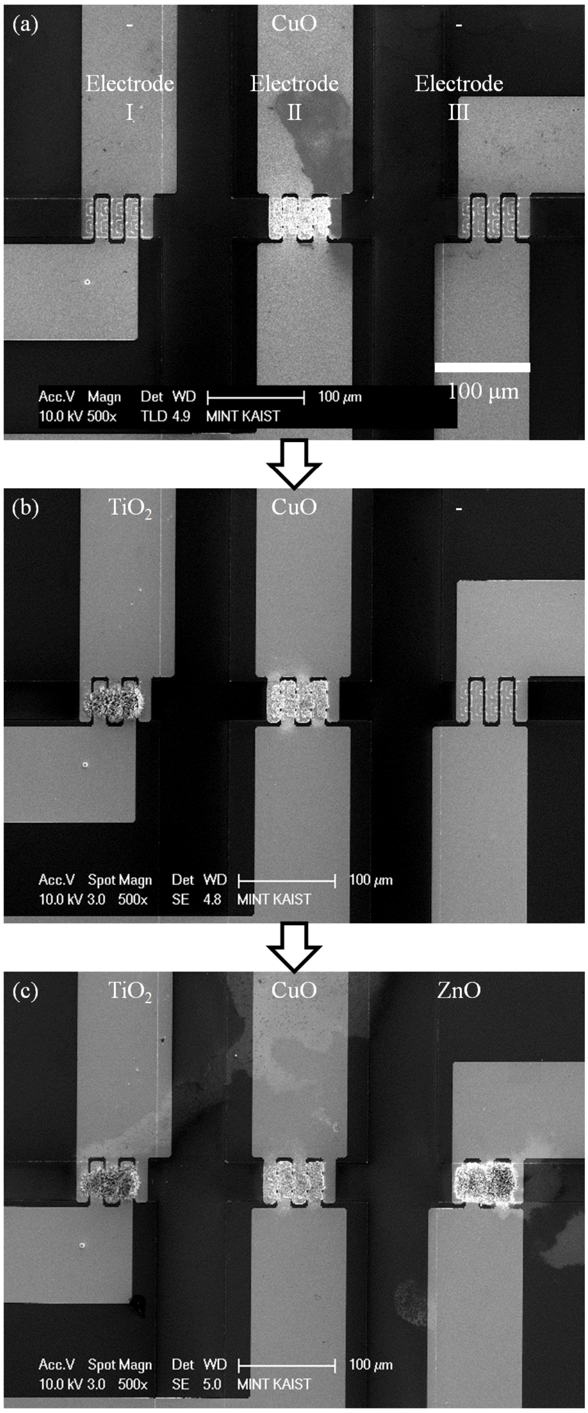

Figure 3: SEM images of the nanostructure array in synthesis sequence: (a) CuO nanowires on electrode-II after step 1, (b) TiO_2 nanotubes on electrode-I after step 2, and (c) ZnO nanowires on electrode-III after step 3.

In step 2, ZnO nanowires were synthesized on the electrode-I with the aqueous ZnO precursor based on 25 mM zinc nitrate, 25 mM HMTA and 6 mM polyethylenimine (PEI) using localized heating. The reaction is similar to synthesis of CuO nanospikes. The synthesis of ZnO nanowires can be described by the following chemical reactions [6]:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (4)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \qquad (5)$$

$$2OH^- + Zn^{2+} \rightarrow ZnO(s) + H_2O \qquad (6)$$

ZnO nanowires on electrode-I were converted to TiO_2 nanotubes by using LPD method with aqueous precursor solution for TiO_2 synthesis with 0.15 M boric acid and 0.05 M ammonium hexafluorotitanate. The device with CuO nanospikes and ZnO nanowires was dipped in the TiO_2 precursor at room temperature. ZnO nanowires were coated with TiO_2 layer and ZnO dissolved simultaneously in the acidic solution. Eventually, the ZnO nanowires were etched out and TiO_2 nanotubes were remained. The synthesis of TiO_2 nanotubes and dissolution of ZnO nanowires can be described by the following chemical reactions [7, 8].

$$TiF_6^{2-} + 2H_2O = TiO_2 + 6F^- + 4H^+ \qquad (7)$$

$$H_3BO_3{+}4HF = HBF_4 + 3H_2O \qquad (8)$$

$$ZnO + 2H^+ = Zn^{2+} + H_2O \qquad (9)$$

Even though ZnO nanowires were dissolved in the TiO_2 precursor, the CuO nanospikes were not affected by TiO_2 precursor.

In step 3, ZnO nanowires were locally synthesized on the electrode-III by using abovementioned method.

These synthesis steps were designed to minimize damage and effect to the pre-synthesized nanomaterials by next synthesis process.

The Figure 3 shows the SEM images of the device after each synthesis step. The Figure 3(a) shows CuO nanospikes on the electrode-II after step 1. The Figure 3(b) shows TiO_2 nanotubes converted from ZnO nanowires on the electrode-I after the step 2. At last, the Figure 3(c) shows ZnO nanowires on the electrode-III after the step 3.

RESULTS AND DISSCUSSION

Analysis of Nanomaterial Device

The Figure 4 shows the SEM images of each nanostructure. Every nanostructure formed stable mechanical and electrical connection between sensing electrodes. The average diameters of TiO_2 nanotubes, CuO nanospikes, and ZnO nanowires were approximately 100 nm, 100 nm, and 50 nm, respectively and their average lengths were about 5 µm, 2 µm, and 5 µm, respectively.

We can find the nanostructure junctions in the SEM images. These junctions can be used as paths for the electrical current during gas sensor operation and play an important role to increase the sensitivity of gas sensor by making numerous necking locations.

We analyzed components of the nanostructures by EDS. The TiO_2 nanotubes contain a few percentages of Zn elements that remained from the conversion process in step 2. CuO nanospikes and ZnO nanowires are pure materials without significant contamination.

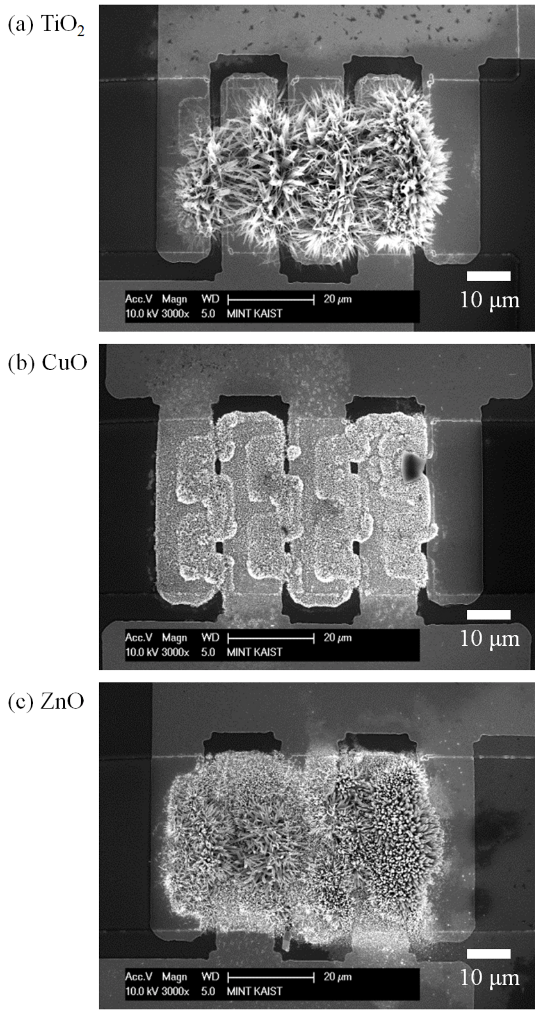

Figure 4: SEM images of (a) TiO_2 nanotubes, (b) CuO nanospikes, (c) and ZnO nanowires

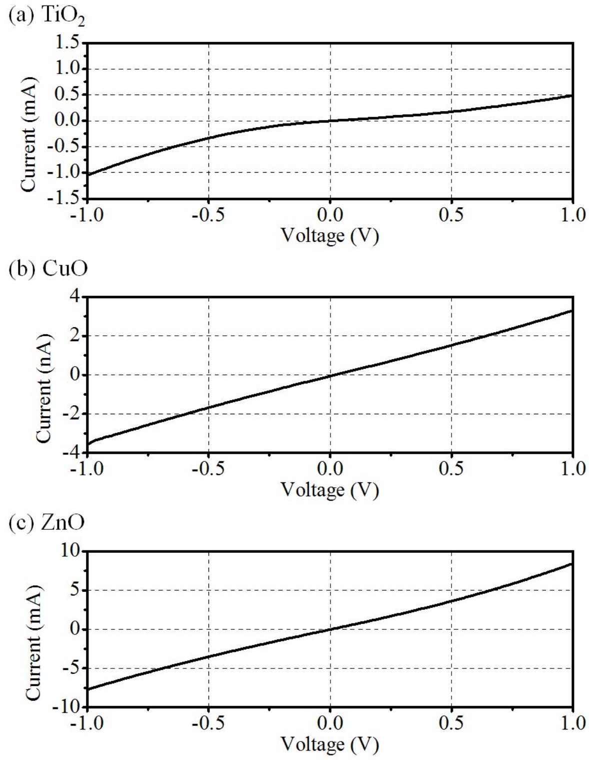

Figure 5: Current-voltage curve of (a) TiO_2 nanotubes, (b) CuO nanospikes, and (c) ZnO nanowires.

The current-voltage curve of TiO_2 nanotubes shows a typical schottky behavior and that of CuO nanospikes and ZnO nanowires show weak schottky behaviors, which represent reliable connections between electrodes and each nanostructure sensing material (Figure 5(a-c)).

CONCLUSION

In summary, we successfully fabricated array of three different nanomaterials (CuO nanospikes, ZnO nanowires, and TiO_2 nanotubes) by using a sequential combination of localized hydrothermal and LPD reaction processes. This method would be very useful for the low-cost and low-power fabrication of multiplexed nanomaterial array. The nanostructures made reliable and controllable connection. The devices fabricated by this method are expected to be used for accurate multiplexed portable gas sensor because of their high sensitivity, selectivity and low-power consumption.

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