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A fast-response/recovery ZnO hierarchical nanostructure based gas sensor with ultra-high room-temperature output response

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ABSTRACT

In this paper, a ZnO hierarchical nanostructure based gas sensor is presented. The proposed implementation features short response/recovery time and ultra-high output response at room temperature (RT). In order to take the advantages of complementary-metal-oxide-semiconductor (CMOS) process in terms of miniaturization and cost-effectiveness, a novel fabrication recipe, consisting of CMOS-compatible techniques, is proposed to form a patterned triple-layer metal, which functions as both interconnection electrodes and catalyst for our reported ZnO hierarchical nanostructure. This enables rapid and local growth of ZnO hierarchical nanostructure directly on a single silicon chip. Reported peak RT output response of 32 (20 ppm NO_2) provides a significant 28-fold improvement over the traditional widely adopted nanowire-based gas sensor. Meanwhile, a time efficient gas sensor is also validated by the presented temporal performance with a response and recovery time of 72 s and 69 s, respectively. In addition, compared with the previously demonstrated gas sensors operating at 200–300 °C, the proposed RT sensing completely removes the power-hungry heater and eliminates the related thermal reliability issues. Moreover, the demonstrated process flow well addresses the challenging issues of the traditional mainstream "drop-cast" method, including poor yield, non-uniformity of device performance and low efficiency caused by inevitable manual microscope inspection.

1. Introduction

In the past decade, nano-material and nano-structure based devices develop rapidly in the gas/chemical sensing area due to their exhibited extraordinary performance [1–5]. Attributed to its large surface to volume ratio [6,7], nano-scale dimension (close to Debye length) [8,9], and rich surface chemistry [10,11], nano-material with linear morphology (so-called "nanowire" (as shown in Fig. 1(a))) was first adopted and a number of nanowire-based implementations have been presented [10,12–16]. Despite the high output response reported for this nanowire structure, heating is still inevitable to maintain a high operating temperature (typically 200–300 °C) [17–22], resulting from the fact that the output response is closely correlated to the operating temperature. Consequently, with this classical nanowire structure, it is quite challenging to obtain a satisfactory response at room temperature (RT). The RT gas sensing is able to completely remove the needed power-hungry heater [23], and shows great promise to the gas sensor's monolithic integration with the complementary-metal-oxide-semiconductor (CMOS) analog/digital circuitries, which are typically operated at RT and thermally vulnerable [24]. This envisioned single-chip solution, featuring on-chip gas sensing/processing in real time, provides us a unique opportunity to take the advantages of low cost and continuing miniaturization of the standard CMOS process.

Additionally, we reported recently that at a temperature of 200 °C, ZnO hierarchical nanostructures (as shown in Fig. 1(b)) with non-linear morphology outperform the classical nanowire structure for their exclusive "self-gating" effect [25]. According to our theoretical modeling, it originates from the dendritic parts showing characteristic potential distribution after the surface chemical reaction with target gas molecules. In order to implement the promising gas sensing/processing system on a single chip, we further explored the ZnO hierarchical nanostructures RT gas sensing performance. Moreover, regarding the hierarchical nanostructures fabrication, several obstacles remain on the way to the aforesaid monolithic integration, including CMOS incompatibility [24], non-uniformity of device performance, and more significantly, extremely poor yield

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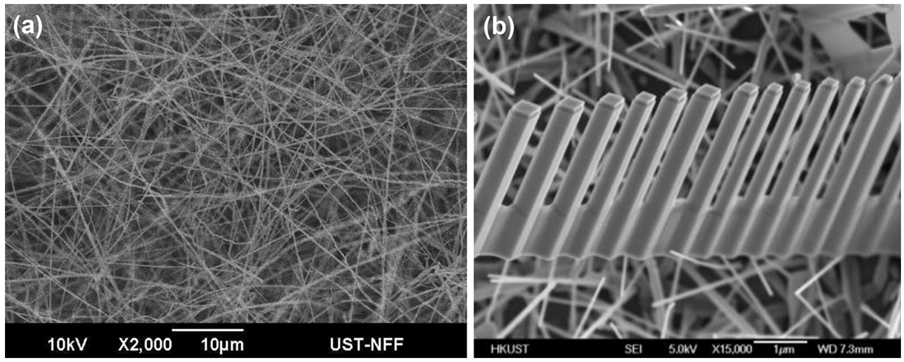

Fig. 1. (a) SEM image of nanowire, (b) zoomed SEM of hierarchical nanostructure.

of the fabricated nano-devices [26]. Generally, the most widely adopted approaches for fabricating nanostructure include chemical synthesis, ultrasonic exfoliation and transfer of the nano-devices onto the target silicon chip with pre-fabricated electrodes, namely "drop-cast" method [27]. This "drop-cast" method, as its name suggests, disperse the exfoliated nano-devices randomly on the silicon chip regardless of their contact quality with the metal electrodes, leading to very poor yield and uniformity. Furthermore, manual inspection with high-resolution microscope is always necessary to select a proper device, making the whole sensing system's mass production unrealistic [28].

In this paper, we report a novel high-yield fabrication approach for ZnO hierarchical nanostructures, which is quite suitable for mass production. The utilized process steps for patterning metal electrodes include standard photolithography, physical vapor deposition (i.e. evaporation) and lift-off, which are all fully CMOS-compatible. Gold catalyst contained in triple-layer metal electrodes is in turn exploited to realize the self-assembled growth of our customized ZnO hierarchical structures, leading to a dramatically improved device yield and uniformity. Furthermore, a case study of NO_2 sensing is chosen to validate our fabricated ZnO hierarchical nanostructure. Reported RT performance indicates that our proposed hierarchical nanostructure greatly outperforms traditional nanowire in terms of output response, response time and recovery time, which paves the way toward a cost-effective monolithic gas sensing/processing chip with ultra-lower power consumption. The remaining of this paper is organized as follows: Section 2 theoretically describes the sensing mechanism of the proposed ZnO hierarchical nanostructure; the detailed fabrication process flow is presented in Section 3; the experimental results are reported and compared with previous literatures in Section 4; the concluding remarks are provided in Section 5.

2. Sensing mechanism

ZnO is known as an n-type semiconductor for its dominant electrons contributed by the oxygen vacancy and Zn interstitial [29]. When exposed to oxidizing gas ambient (e.g. NO_2), the surface adsorbed NO_2 molecules captures electrons from the ZnO conduction band [30,31]. As a result, the induced surface depletion region is expanded and the overall resistance is increased. Based on this principle, traditional planar ZnO film was first utilized to make discrete electronic device for gas sensing applications. The planar ZnO film exhibits poor response due to its limited surface to volume ratio. For the large output response dependence on the operating temperature, heating was found to be an effective way to increase the response without considering the power consumption issue [32]. In order to take the advantage of the standard CMOS process's fast miniaturization trend, it is attractive to integrate the discrete ZnO film sensor on chip. The primary and most challenging issue is how to address the heating associated huge power consumption and meet the extremely limited on-chip power budget. ZnO nanowire based implementations were reported later to significantly improve the surface to volume ratio as well as the output response, which makes it possible to lower the required operating temperature and reduce the power needed for heating. Featuring nano-scale dimension close to the width of the surface depletion region, any change of the nanowire's surface depletion region width can cause much larger resistance variation, which corresponds to much higher output response. However, this improvement is still not enough to make the nanowire work properly with the operating temperature down to 25 °C (i.e. RT).

In this section, novel hierarchical nanostructures (Fig. 1(b)) are proposed to further extend the upper-limit of the response [25], especially the one at RT. As illustrated in Fig. 2(a), the proposed hierarchical nanostructure exhibits a unique morphology with "backbone" and "teeth" regions. Recently, we reported a "self-gating" effect based on the simulation of the internal electric field distribution of the hierarchical nanostructure [25]. Compared to the conventional nanobelt device with same dimension, shown in Fig. 2(c), it has been proven that that the conducting path at the "backbone" area can be manipulated by the "teeth" region, which results in a significantly improvement of gas sensing performance [25]. In addition, according to classical gas sensing mechanism and surface vacancy defect model [33,34], oxygen vacancy defects on the surface of the nanomaterial adsorb oxygen molecules of NO_2 and capture free electrons during this reaction. Meanwhile, these vacancy defects function as acceptors that reduce the free electron concentration and form electron depletion region at the surface (Fig. 2(d)). Specifically, it is found that a negative potential is formed between the source and the drain at the edge of the nanobelt surface (Fig. 2(d)). Moreover, the conduction path of this nanobelt device is narrowed due to the reaction between the NO_2 molecules and surface vacancy defects. As presented in Fig. 2(b), for the proposed hierarchical nanostructure, electrons are accumulated at the surface of "backbone" region as well as "teeth" region. Resulting from the nano-scale dimension, a huge potential drop can be formed at the "teeth" part. Consequently, the electric field distribution inside the "backbone" region is dramatically affected, which further narrows the aforesaid conduction path. In ref. 25, the simulation results have shown that the proposed hierarchical nanostructure's conductance differs from that of the nanobelt by one order of magnitude when exposed to the NO_2 gas. Furthermore, it is worth pointing out that the significant sensing performance improvement also attributed to its unique electron transport mechanism. Specifically, resulted from the surface trap states, the equivalent energy