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A highly selective chemical sensor array based on nanowire/nanostructure for gas identification

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ABSTRACT

Real-time detection and identification of multiple gases based on a single-nanowire sensor array have been investigated. We present the fabrication, characterization, and sensing performance of a single-nanowire array consisting of four different materials from three categories, which are metal (palladium), conducting polymer (polypyrrole and polyaniline), and semiconductor (zinc oxide), on a chip via a site-specific electrochemical deposition process. The presented nanowire array on a single chip has been used to detect and identify four target gases including hydrogen, methanol, carbon monoxide, and nitrogen dioxide. Each single nanowire shows an excellent sensitivity at room temperature, and a sub-ppm (parts per million) detection limit is achieved. The identification of these four targets has been successfully demonstrated with the help of principal component analysis. Our study shows that this single-nanowire sensor array is able to not only accurately distinguish four targets but also roughly estimate the target concentration, forming a basis for an electronic nose with far-reaching applications.

1. Introduction

An electronic nose (e-nose) that mimics the olfaction system in mammals is expected to be applied to a wide range of areas, such as disease diagnosis, food quality inspection, gas chromatography, and spacecraft atmospheric monitoring [1–5]. These applications require that the e-nose not only detects an individual target at extremely low concentration (down to ppm or lower), but also identifies the exact chemicals of the target with high selectivity. In order to improve sensitivity, previous studies employed nanomaterials, such as nanowires and nanoparticles, as e-nose building blocks because of their high surface area to volume ratio and superior sensitivity for detecting volatile organic compounds (VOCs) and toxic industrial gases (e.g., NO_2 and CO) [6,7]. Target identification, on the other hand, was mainly realized by including an array of different sensor elements to build a sensor array as the base for the e-nose device [8,9].

Despite previous success in gas detection, the reported sensor array based e-noses suffer from several drawbacks that seriously limit their applications. First, the active materials in the sensor elements are usually limited to one type of material, such as metal oxides and conducting polymers [7–9]. This limitation restricts the variety of sensible target molecules of the sensor array, thus rendering it a device only applicable to specific targets. In addition, the similar chemical properties among the active sensing materials in the array can result in a less than optimal selectivity. For example, a reported sensor array based on only conducting polymer nanowires failed to clearly identify two of the target VOCs [10]. Second, the previous nano sensor array studies were satisfied with distinguishable sensing patterns but did not attempt to verify the sensor performance in real situations or explore the possibility of concentration estimation. For advanced cases, such as spacecraft monitoring, where both the compositions and the concentrations of targets need to be identified, the ability of the sensor array to estimate the target concentration becomes extremely important.

In this work, we present a site-specific electrochemical deposition method to incorporate an array of single nanowires on a single chip. The incorporation of four single nanowires – palladium (Pd), polypyrrole (PPy), polyaniline (PANI), and zinc oxide (ZnO) – from three material types – metal, conducting polymer, and metal oxide – into a sensor array is demonstrated for the first time. The developed sensor array in this research is able to detect four gases with distinct properties, including carbon monoxide (CO, a very common household toxic gas), hydrogen (H_2, an important potential energy source), methanol (CH_3OH, a representative VOC), and nitrogen oxide (NO_2, a common oxidizing gas and a common industrial toxic gas), and well-separated sensing patterns are built up with the help of principal component analysis (PCA) for all targets, even at

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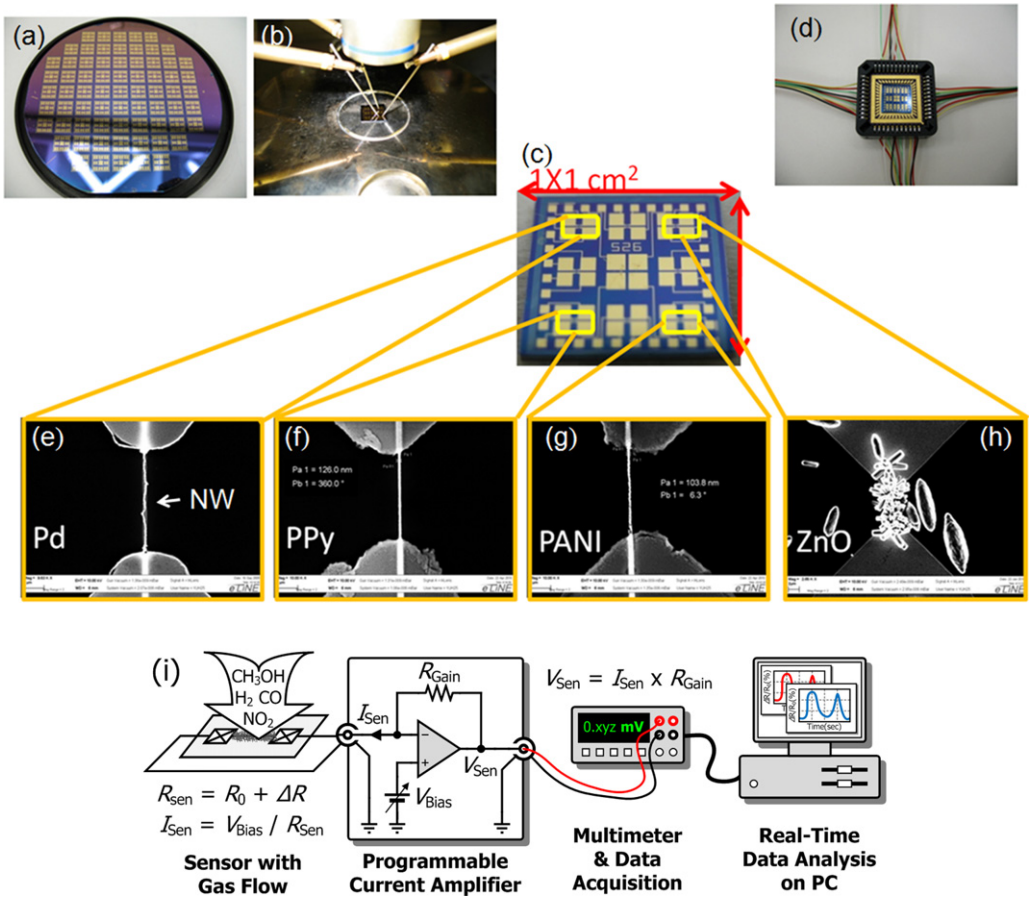

Fig. 1. Nanowire fabrication process and SEM images of synthesized single nanowires. (a) 4-in. Si wafer containing 69, 1 cm × 1 cm chips. (b) A chip placed under three probes of a probe station during nanowire electrochemical deposition. (c) Chip containing four different single nanowires. (d) Sensor chip built on a chip with a single-nanowire array after wire bonding and integration. (e–g) SEM images of Pd, PPy, and PANI single nanowires, respectively. The bright thin line denotes the nanowire, and the bright areas on top and bottom denote Ti/Au electrodes. (h) SEM image of ZnO nanowire. (i) Measurement setup for the read-out of sensor signal.

extremely low (sub-ppm) concentrations. Finally, a blind experiment where the sensor array was exposed to four gas injections with unknown compositions and concentrations was conducted to verify the identification ability. We found that, by comparing each injected target with the original sensing patterns, the target composition can be successfully identified and, moreover, approximated with the accuracy determined by calibration (data collected to build up sensing patterns) PCA data point density. Therefore, the sensor array synthesis and systematic analysis performed here not only provide a feasible way of incorporating nanowires from different material types on a single chip, but also point out a way for target concentration estimation through PCA.

2. Experimental

2.1. Template preparation and nanowire synthesis

The single Pd, PPy, and PANI nanowires were electrochemically deposited inside predefined PMMA nanochannels on top of a silicon (Si) chip. A p-type 4-in. Si wafer with a thin layer of SiO_2 (100 nm thick) was chosen as the substrate. After photolithography and e-beam evaporation, a total of 69 chips of 1 cm × 1 cm size were defined on top of the wafer, and each chip consisted of 16 pairs of Ti/Au working electrodes and 4 Ti/Au gate electrodes. A layer of 100 nm thick PMMA was then spun on the wafer surface, while e-beam lithography was used to direct-write single nanochannels with adjustable width (typically less than 100 nm) across each Ti/Au working electrode pair. Because the distance between the working electrodes decides the actual length of nanochannels, both the width and length of the nanochannels can be predefined.

2.2. Nanowire synthesis

Fig. 1 illustrates the fabrication process of a nanowire sensor array on a chip. After template preparation, the 4 in. wafer with patterned electrodes and nanochannels (Fig. 1(a)) are cut into small slices, and four different single nanowires are grown electrochemically with a probe station (Fig. 1(b)) on top of these 1 cm × 1 cm chips (Fig. 1(c)) using different electrolyte solutions. Each chip had 16 pairs of working electrodes with one nanochannel across each pair. Four gate electrodes were positioned in the center of the chip to maximize the field effect. The purpose of adding gate electrodes was to better control the nanowire growth by applying a vertical electric field underneath the channel, as discussed in our previous studies [11,12]. A probe station (Micro Manipulation Co. Inc.) with three probes was used to make direct contacts with the electrodes. Two of the probes were connected with a pair of working electrodes, while the third one was connected with one of the gate electrodes. A small drop of electrolyte solution was placed on top of the nanochannel, while a semiconductor analyzer (Agilent B1500A) was employed to provide a constant current signal through the working electrodes and a constant voltage signal through the gate electrode. No heating element was used during growth and growth temperature was kept at room temperature (27 °C). Once the nanowire growth was complete, all the electrical signals were turned off, and the remaining solution was blown