Gas Sensor Array Based on Metal-Decorated Carbon Nanotubes

Alexander Star,* Vikram Joshi, Sergei Skarupo, David Thomas, and Jean-Christophe P. Gabriel †

Nanomix Inc., Emeryville, California 94608

Received: July 11, 2006; In Final Form: August 21, 2006

Here we demonstrate design, fabrication, and testing of electronic sensor array based on single-walled carbon nanotubes (SWNTs). Multiple sensor elements consisting of isolated networks of SWNTs were integrated into Si chips by chemical vapor deposition (CVD) and photolithography processes. For chemical selectivity, SWNTs were decorated with metal nanoparticles. The differences in catalytic activity of 18 catalytic metals for detection of H₂, CH₄, CO, and H₂S gases were observed. Furthermore, a sensor array was fabricated by site-selective electroplating of Pd, Pt, Rh, and Au metals on isolated SWNT networks located on a single chip. The resulting electronic sensor array, which was comprised of several functional SWNT network sensors, was exposed to a randomized series of toxic/combustible gases. Electronic responses of all sensor elements were recorded and the sensor array data was analyzed using pattern-recognition analysis tools. Applications of these small-size, low-power, electronic sensor arrays are in the detection and identification of toxic/combustible gases for personal safety and air pollution monitoring.

Introduction

Sensor arrays, which are often called electronic noses, mimic nature by combining artificial computational capability and pattern-recognition based sensing architectures.¹ A sensor array achieves selectivity by providing a characteristic signature for an analyte derived from the global response of the sensors contained within the array. To date, sensor modalities include surface acoustic wave and bulk resonating quartz crystal devices, micromachined cantilevers, conducting polymers, semiconducting metal oxide resistors, chemically sensitive field-effect transistors (FETs), and carbon-black-polymer composites.² Miniaturization of sensor elements is important for the design of high-density sensor arrays with relatively small spatial footprints. Recently, electronic devices utilizing active elements made of nanowires³ and carbon nanotubes⁴⁻¹⁰ have been shown to function as extremely sensitive and small chemical sensors. Integration of these sensor elements into a complex sensor array may bring about electronic noses as complex as the mammalian olfactory system.¹¹

The basic concept of chemical gas detection using a carbon nanotube field-effect transistor (NTFET) is illustrated in Figure 1A. Single-walled carbon nanotubes (SWNTs) integrated into a Si platform have a characteristic electrical conductance that can be measured by applying a voltage. As an analyte comes into contact with the SWNT, network conductance is modified to produce a detection signal. Specific sensitivity of NTFET sensors can be achieved by employing recognition layers, which induce chemical reactions that modify the NTFET device characteristics. This sensing design recently has been demonstrated for detection of various chemical and biological analytes.^{6-10,12} In particular, a catalytic metal (Pd) was used to

decorate SWNTs toward detection of H_2 and CH_4 at ambient temperatures.^{6,8}

Thermal and electron-beam evaporation previously have been used for metal deposition on sidewalls of SWNTs.13 Electrochemical deposition, compared to other methods, offers significantly higher control over the purity and the amount of material deposited onto the nanotube surface.¹⁴ To date, several procedures have been published¹⁵ for the electrodeposition of noble metals on SWNTs under direct potential control. Choi et al. has reported¹⁶ spontaneous metal deposition on SWNT sidewalls, creating a simple and elegant technique to produce metal-decorated carbon nanotubes. However, this method could not allow any site-specific metal deposition on a device chip, and precise deposition of metal species at specific locations is a requirement for the fabrication of a sensor array. Site-specific metal deposition can be accomplished using electrochemical galvanic displacement^{17,18} by (1) connecting a specific nanotube device to a metal substrate having a red./ox. potential far lower than the metal to be deposited, and (2) immersing the device into a solution of the metal cation to be reduced and deposited. This closes the circuit of an electrochemical cell and induces metal deposition on nanotube surfaces upon application of an appropriate potential. Through the use of this method, selected NTFET devices can be decorated with metal nanoparticles of different catalytic metals (Au, Pt, Pd, Rh, etc.) while leaving other devices unmodified on a single chip.

In our study, we expanded evaporation and electrodeposition approaches for detection of important toxic/combustible gases by using a sensor array approach. We elucidated the nature of NTFET sensing by comparing the performance of different catalytic metals and demonstrated a sensor array based on crosssensitive NTFET sensor elements decorated with different catalytic metals. In addition, we compare the sensitivity of metaldecorated nanotubes produced by evaporative and electrochemical methods and discuss the applicability of both as components in nanoscale sensor arrays.

10.1021/jp064371z CCC: \$33.50 © 2006 American Chemical Society Published on Web 10/04/2006

 $^{^{\}dagger}$ This article is dedicated to the memory of Dr. Lucy M. Bull, loving wife of Jean-Christophe P. Gabriel.

^{*} To whom correspondence should be sent at the present address: Department of Chemistry, University of Pittsburgh. E-mail: astar@pitt.edu.