Hydrogen detection by individual Pd-modified ZnO nanowire

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***Abstract* — In this work an individual Pd-modified ZnO nanowire (Pd/ZnO NW) was integrated into a nanosensor device using focused ion beam (FIB)/scanning electron microscopy (SEM) system. The Pd/ZnO arrays were synthesized by electrochemical deposition. Both ends of Pd/ZnO NW were connected by Pt complex to Au/Cr pads forming a two-terminal device with Schottky contacts. The fabricated nanodevice shows high performance gas sensing properties at room temperature with the response of ~ 1700% to 1000 ppm hydrogen. The methodology and principle illustrated in this research can be extensively applied to other individual nanostructures of different materials in a wide range of applications.**

***Index Terms* — nanosensor, gas sensor, Pd/ZnO, electrochemical deposition, hydrogen.**

I. INTRODUCTION

Due to high surface to volume ratio, the electric transport in conduction channel of one-dimensional (1-D) nanostructures of metal oxides, including nanowires (NWs), nanobelts, nanotubes, nanorods, and nanofibers is very sensitive to surface reactions [1]. Therefore, 1-D nanostructures are widely investigated for highly sensitive biological and chemical detection [2]. The most widely used semiconducting oxides are *n*-type SnO_2 and ZnO nanostructures due to low-cost of synthesis and high sensitivity to a series of reducing (ethanol, H_2, CO, acetone, etc.) and oxidizing (NO_2, NO, SO_2, etc.) gases. However, these pristine structures have shown low selectivity to specific gases. This drawback usually limits their practical application. Therefore, different approaches are implemented to increase the selectivity of sensors, such as doping, surface functionalization, hybridization with other metal oxides, etc [3]. The doping and surface functionalization with noble metals (Pd and Pt) was found to be very efficient in order to increase the selectivity to hydrogen gas, even at room temperature [3]. In this work, the individual Pd-modified ZnO NW was connected to Au/Cr pads in order to fabricate a two terminal device, which demonstrated high sensitivity to H_2 gas at room temperature, which is an advantage of such nanosensor.

II. EXPERIMENTAL

Pd/ZnO NW arrays were deposited on FTO (SnO_2:F)/glass substrate via an electrochemical deposition as was reported previously [4]. The synthesis was performed at relatively low temperature (< 90 ºC). The Pd-modification was achieved by adding $PdCl_2$ solution (1.25 µM) in the electrolyte solution. The morphological, structural and chemical properties of material were reported in detail in another paper [5]. The gas sensing properties were investigated at room temperature as was describe previously at 30% relative humidity [4]. The gas response was defined as ratio of currents under exposure to H_2 gas (I_{gas}) and in the air (I_{air}).

III. RESULTS AND DISCUSSIONS

Fig. 1(a,b) show SEM images of Pd-modified ZnO NW arrays at different magnifications. Pd/ZnO NWs grow homogenously and uniformly on the FTO substrate with density of ~ 8 NW/µm^2. The energy dispersive X-ray spectroscopy (EDX) measurements showed the 0.68 at% content of Pd in deposition. The diameter (D) of NWs is in the range of 100 – 400 nm (measured using top view images), while the length (*L*) is in the range of 1 – 3 µm, measured in cross-sectional images, (not shown).

Fig. 1(c) shows the XRD diagram of Pd/ZnO NW arrays recorded in the range of 10 – 80º. In this diagram only reflections corresponding to wurtzite ZnO (PDF#00-036-1451) and to tetragonal SnO_2 (PDF#01-088-0297) were detected, which originate from FTO substrate [4] and are marked with red (*). No peaks attributed to Pd or Pd-oxide were detected in these deposits/samples.

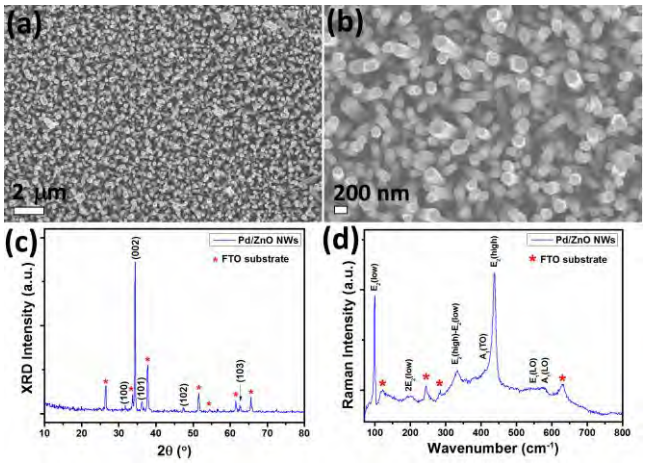

Fig. 1. (a,b) SEM images of Pd-modified ZnO NWs array deposited on FTO substrate. (c) XRD and (d) room temperature micro-Raman spectra of Pd/ZnO NW.

Fig. 1(d) shows the room temperature micro-Raman spectra of Pd/ZnO NWs. Peaks marked with red (*) were assigned to the FTO substrate [4]. Peaks at 100 cm^{-1} and 438 cm^{-1} were assigned to E_2 (low) and E_2 (high) non-polar

optical phonon modes, typically for wurtzite structure of ZnO [5]. The peaks at 204, 333, 377, 575 and 582 cm^{-1} were assigned to E_2 (low) second order mode, E_2 (high)–E_2 (low) multi-phonon scattering, A_1 (TO), E_1 (LO) and A_1 (LO) modes, respectively.

Fig. 2(a) shows the SEM image of two-terminal device based on individual Pd/ZnO NW. The radius of Pd/ZnO NW is ~ 230 nm. The NW is placed on SiO_2 layer of chip and the both ends are contacted with Pt complex to Au pads. The fabrication of nanosensor using FIB/SEM system is described in detail in other works [4, 5]. The typical current – voltage characteristic of a device at room temperature is presented in Fig. 2(b). The non-linear behavior indicates on formation of double Schottky contacts due to higher work function of Pt (ϕ = 6.1 eV) compared to electron affinity of ZnO (E_a = 4.5 eV) [4, 5].

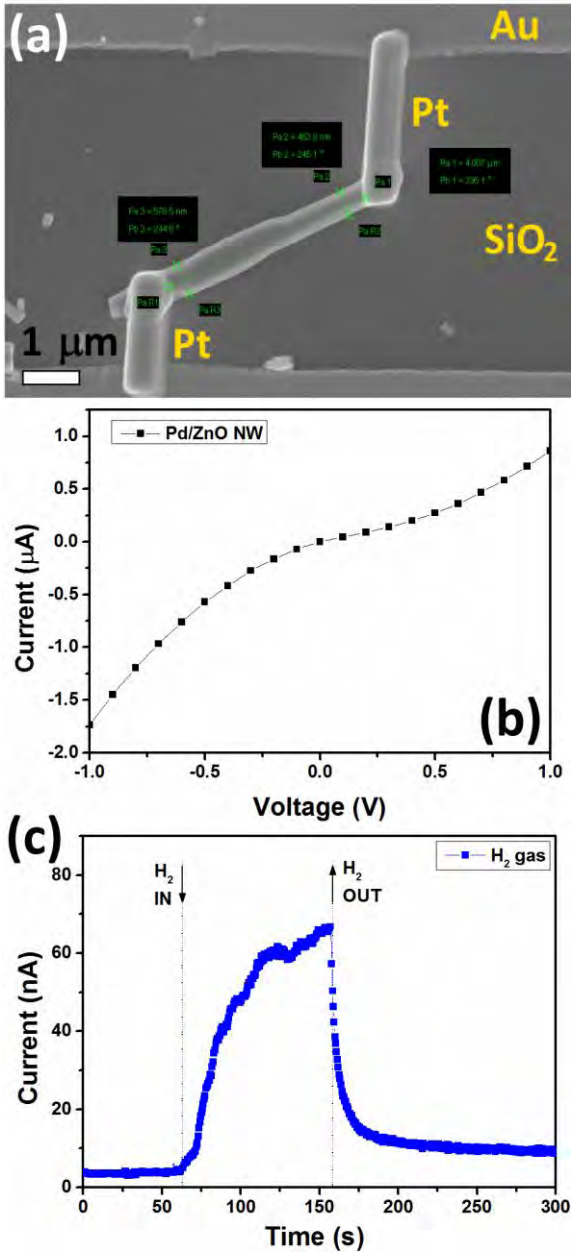

Fig. 2. (a) SEM image of device based on individual Pd/ZnO NW. (b) Room temperature current – voltage characteristic of this device. (c) Dynamic gas response to 1000 ppm of H_2 gas of Pd/ZnO NW at room temperature.

The dynamic gas response of device to 1000 ppm of H_2 gas at room temperature is presented in Fig. 2(c). The calculated gas response is ~ 17×100%, which is higher compared to undoped or Ag-doped ZnO NW [4], demonstrating the efficiency of Pd doping/functionalization of ZnO NWs. The response time (defined as the time necessary to reach a 90% of full signal) is ~ 50 s, while recovery time (defined as the time necessary to recover the 90% of signal) is ~ 100 s. The enhanced performances compared to undoped ZnO NW can be explained based on presence of Pd nanoclusters which is known to have higher catalytic activity at room temperature compared to ZnO and to easily adsorb H_2 forming PdH_x [3, 5]. The detailed gas sensing mechanism is presented in our previous work [5].

IV. CONCLUSION

In this research paper the individual Pd-modified ZnO NW with diameter of ~ 460 nm was successfully integrated into a device using a FIB/SEM system. The fabricated two-terminal device showed high gas response of ~ 1700% to 1000 ppm of H_2 at room temperature. This work demonstrates that individual structures can be used for ultra-sensitive gas sensing applications at room temperature. The described method can be also applied for nanostructures of other materials.

ACKNOWLEDGMENTS

Dr. Lupan gratefully acknowledges CNRS Council for support as expert scientist at IRCP Chimie ParisTech, Paris. Professor Dr. Kienle (CAU, Kiel, Germany) is acknowledged for fruitful discussions and for his help with TEM experiments. This work was partially financially supported by the STCU under the Grant no. 6229.

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