Supporting Information

Manuscript title: Decorated CNT based-on Porous Silicon for Hydrogen Gas Sensing at Room Temperature

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S1

Sensor fabrications were progressed using substrates of P-type Si wafers with thickness of about 330 μm and with resistivity in the range of 0.5-1.5 Ωcm. EA process was employed to prepare chemical media to pursue the etching process. The electrolyte consisted of ethanolic-based solution of hydrofluoric acid (40%) and deionized water (DI). For this given application, we found the optimized conditions for anodization process came in previous experience [20]. In this regard, we prepared electrolyte in the given volume ratio of (40% HF: EtOH; 1: 1) and pursue EA process under condition of 10 mAcm^{-2} for 10 minutes. The electrochemical process established continuously; employing direct current.

Palladium nanoparticles were deposited as catalyst over the etched surface, by electroless technique. The Pd nanoparticles were synthesized using diluted aqueous solution of $PdCl_2$ in the presence of HCl (trace) at Room temperature (RT). The concentrations of $PdCl_2$ and HCl in the solution were 1.13×10^{-3} M and 1.21×10^{-3} M, respectively.

Following, the CNTs was grown over porous wafers using CVD technique. This operation was carried out using CH_4 (feed gas) with a flow rate of 80 sccm for 40 min at 970 °C [21]. Subsequently, the resulted samples (porous silicon/CNTs) decorated with Pd nanoparticles; using the same electroless process. To reduce the Pd cation, some defects were defined over grown CNTs; using Dimethyl-formamide.

In this way our triple sensor, as first class (C1) was fabricated. Also triple system, as second class (C2), was fabricated in similar procedure except that higher level of Pd catalysis was defined to the initial porous silicon.

S2

The characterizations of samples were measured at room temperature by Sanowa multimeter. Schematic drawing of the electrode geometry for measurements is shown in figure S1. The Schottky contacts were produced by thermal evaporation of Al and Ag paste in the front of the PS surface, respectively.
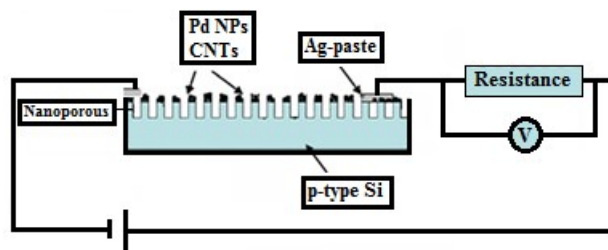

Electrode schematic for electrical measurement

S3

Gas sensing was performed using 4% H_2/N_2 capsule as a testing gas with dry air as a carrier gas at constant flow rate of 500 cc/min. The sensor response to H_2 was measured in exposure to various concentrations (0.2%, 0.3%, 0.4%, 1.5 and 2%). Also, the reproducibility was examined through 3 times repetition of measurements for each concentration. The response of as-prepared sensor was recorded after that stable output under bias voltage was achieved. The time-programmed system introduced 10 min for detection and 20 min for recovery. The test sequence was performed for three cycles under the ambient conditions (temperature: 18 °C ± 1 °C, pressure: 1.0 ± 0.05 bar, and atmospheric relative humidity: 20% ± 10%). Due to experimental limitations, the effect of relative humidity on the response properties is not included in this study.

S4

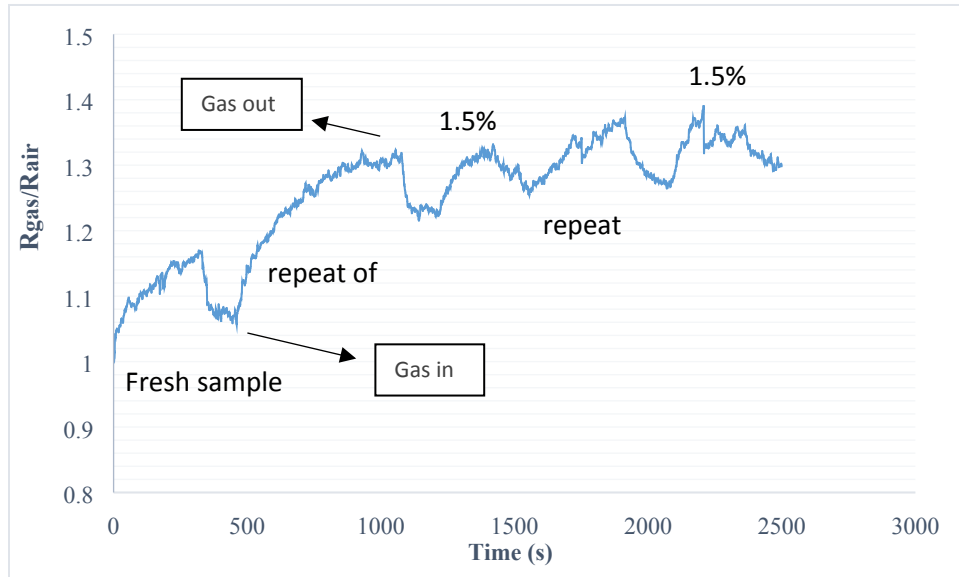Figure S4 shows the EDS characterizations for C1 and C2, respectively.
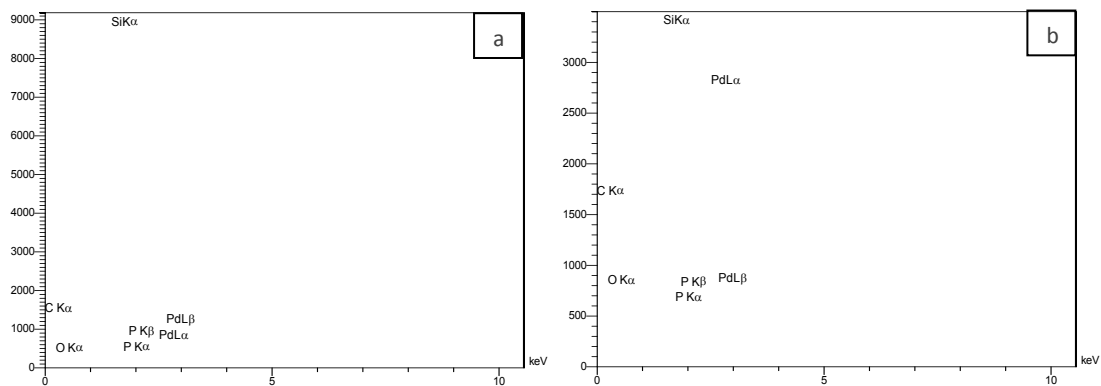
Clearly, S4 (a) demonstrates lower amount of carbonaceous (CNT) and palladium, compared to S4 (b). This could be attributed to the lower electroless duration; consequently, lower catalysis would be available for CVD process; thereby, poor growth of nanotubes is derived, in the case of C1. In this regard, the lower effect of tip growth, as discussed in FESEM images, can be recognized.

## S5

In this graph, you have 3 times repeat of response to 2% H_2 for fresh sample, first cycle and second cycle. Naturally, the fresh sample behaves roughly different from the rest of cycles. It seems the sensor reaches to a stable response by repeating the sensing in 3 cycles for 2% and two times for 1.5%.

The noises at the measurements could attribute to the possible shocking, when the concentration is adjusted for a further measurement. Also, environmental phonons should be considered, too.

S6

Figure S5 demonstrates the variation of reciprocal of the response time by hydrogen concentrations for C1 and C2. It shows that the reaction rate linearly depends on hydrogen concentrations. At the initial stage of the characterization, the rate is $k_a P(1-\theta)^2$, where term of $(1-\theta)^2$ is negligible. Thus, the adsorption rate is approximately $k_a' P$; consequently, the reciprocal of the response time corresponds to the r_a. As demonstrates in the figure S3, the adsorption rate correlates linearly to the hydrogen concentration, which reveals that sensing kinetics of the systems mainly depended on the hydrogen dissociation process of palladium. However, the minor deviations translate the role of beneath layer of CNTs. As mentioned hydrogen chemisorbed in defects and tips of CNTs; consequently, due to irreversibility of chemisorption, it cannot be reflected, perfectly.
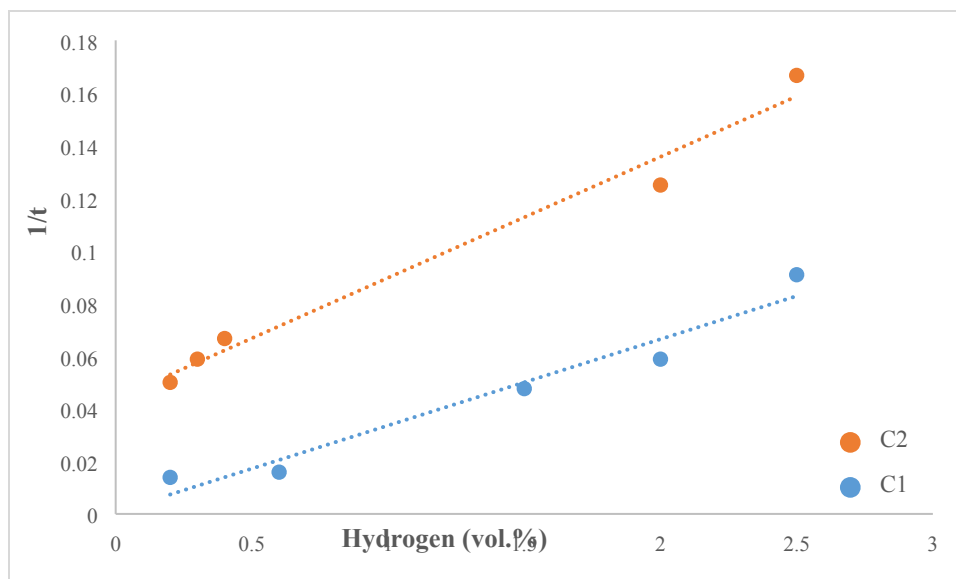
S7

The recorded response is a resultant effect of removal of oxygen layer formed over Pd particles and subsequent volume expansion of the Pd lattice. First, the spillover oxygen atoms accumulate on the surface of active palladium nanoparticles through saturating the dangling bonds. In fact, Pd nanoparticles (and slightly porous silicon, both uncovered area and the area beneath CNTs) adsorb oxygen to reduce their surface activity; this phenomenon occurs over the tips and boundary. In the absence of hydrogen, a layer of charged oxygen species covers the surface of palladium. It was proved that this structure possesses a definite high resistance, which reveals that electron path is complete; indeed, the presence of O^- and O^{2-} in the layer propose the complete circuit.
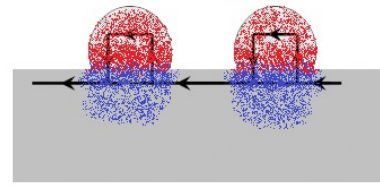
When hydrogen gas flows, the oxygen species carried away by the carrier gas as water molecules. Hydrogen molecules adsorb on the vacant surface sites and dissociate. Overall, substitution of oxygen species with hydrogen atoms as well as receding of formed-water molecules have no substantial interference on the response, since Pd has much higher affinity for hydrogen than water molecules. These hierarchical processes result in the formation of palladium hydride.

S8

Regardless to CNTs, the distributed Pd nanoparticles play great role in enhancement of the resistance.
The diode behaviour of Pd/porous silicon has been studied. The investigation of electrical behaviour shows that, near a Pd grain, the current pathway may demonstrate an alternative. It passes through the schottky barriers of Si-Pd (due to lower resistivity of Pd nanoparticles in comparison with porous silicon), traverses in Pd grain and returns to the porous silicon by passing through the same schottky barrier in the reverse direction. The equivalent circuit is shown in figure below. Once hydrogen is exposed to the system, hydrogen species associated with the Pd grains and is devised within the Pd lattice. Thereby, a dipole layer (right) may form at this region and cause an additional increase in the energy barrier height at the interface. This phenomenon is defined through reduction of current flow, consequently, higher resistance is loaded over system.

Formation of dipole layer between H-Pd and porous silicon
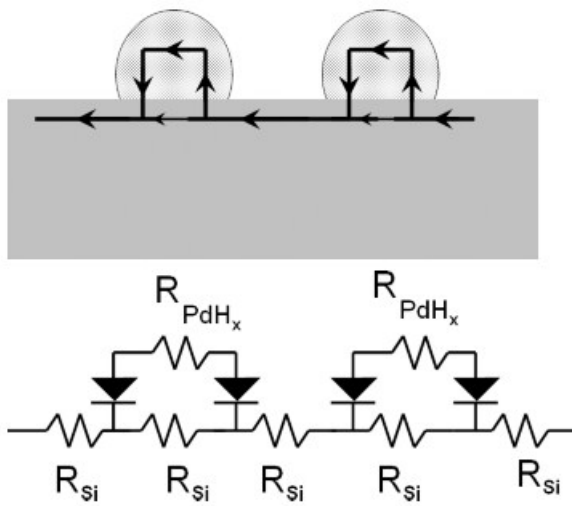
Current pathway in the system of Pd/porous silicon