Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information for

High performance vertical hydrogen sensors using Pd-coated rough Si nanowires

Jin-Seo Noh[1], Hyunsu Kim[1], Beom Seok Kim[2], Eunyeung Lee[1], Hyung Hee Cho[2] and Wooyoung Lee[1,*]

[1]*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, South Korea*

[2]*Department of Mechanical Engineering, Yonsei University Seoul .120-749, South Korea*

INDEX

1. Detailed Structure of Pd-coated Rough Si NWs

In order to closely investigate the overall shape of Pd-coated rough Si NWs, an excess of Pd were deposited on rough Si NWs. **Figure S1**(a) shows SEM images of rough Si NWs coated with 600 nm thick Pd. The thickness was not selected for the best hydrogen-sensing capability, but for magnifying Pd film profile along the length of the Si NWs. It is seen from the full-covering image (top one) of Fig. S1(a) that the nanowires are too densely placed to be discernible. Therefore, the top (1), middele (2), and bottom (3) parts of the nanowires were closed up, as shown in a column in Fig. S1(a). Now it is found that the average thickness of the Pd-coated Si NWs becomes thinner from top to bottom, revealing most Pd is concentrated on the upper part of the nanowires. Even for the Si NWs coated with this thick Pd film, the bottom thickness of the nanowires appeared to be the almost same as that for pure Si NWs at the same position. Similar analyses were performed on rough Si NWs coated with 7 nm thick Pd and the results are displayed in **Fig. S1**(b). Although the thickness variation is not as pronounced as for 600 nm thick Pd, it is still conceivable that the average thickness is slightly larger at the top than at the rest of the nanowires. These observations suggest that the Pd-coated Si NWs resemble an inversely tapered baseball bat and the current flow along the Pd surface from the top of the nanowires to the substrate is negligible

2. Hydrogen-Sensing Properties of Pure Rough Si NWs and Pd Thin Films

Figures S2(a) and (b) show the hydrogen-sensing properties of pure rough Si NWs and a 7 nm thick Pd thin film depositied on the Si substrate. We conducted the test at 2% H_2 in air. As shown in Fig. S2(a), pure rough Si NWs do not respond to H_2, revealing that the rough Si NWs can not function as a hydrogen sensor by themselves. On the other hand, a 7 nm thick Pd thin film shows characteristic response cycles to H_2, as can be seen in Fig. S2(b). However, the response is a typical resistive behavior, in which the resistance increases upon H_2

exposure due to increased carrier scatterings by absorbed hydrogen atoms. This is a sharp contrast to semi-On-Off response behaviors observed in Pd-coated rough Si NWs. Moreover, the sensitivity of this pure Pd film is below 10% even at 2% H_2, which is far lower compared to Pd-coated rough Si NWs.

3. Step-by-Step Changes of Nanowire Surface Profiles

Figure S3(a) shows a magnified SEM image of as-prepared pure Si NWs. The nanowires have rough surfaces enough to be called rough Si NWs. The rough surface morphology is transferred to Pd-coated Si NWs, when a Pd thin film is coated on the surface of Si NWs. This is clearly observed in **Fig. S3**(b) for Si NWs coated with 7 nm thick Pd film. The rough surface profile of Pd significantly increases surface area and imperfections per unit volume, leading to a substantial increase in both sensitivity and response time. Once the Pd-coated rough Si NWs undergoes annealing at 150 ^{o}C for 3 hours, their rough surfaces become smooth and imperfections like grain boundaries are cured much, as demonstrated in Fig. 3(c). This is likely to lead to a drop in sensitivity.

4. Hydrogen-Sensing Properties of Annealed Pd-coated Rough Si NWs

We measured the hydrogen-sensing properties of Pd-coated rough Si NWs that passed through annealing at 150 ^{o}C for 3 hours. **Figure S4** shows response curves of the annealed rough Si NWs coated with 7 nm thick Pd. As expected above, the sensitivity decreases to about 115% at 2% H_2. This result is attributed to the surface smoothening of the nanowires and the partial healing of imperfections during thermal annealing, which reduce the number of hydrogen accommodation sites. In addition to this, the H_2 gas detection limit is increased to 50 ppm. We think that this is also related to the surface smoothening of the nanowires and the consequent minute increase of distance between nearest nanowires.

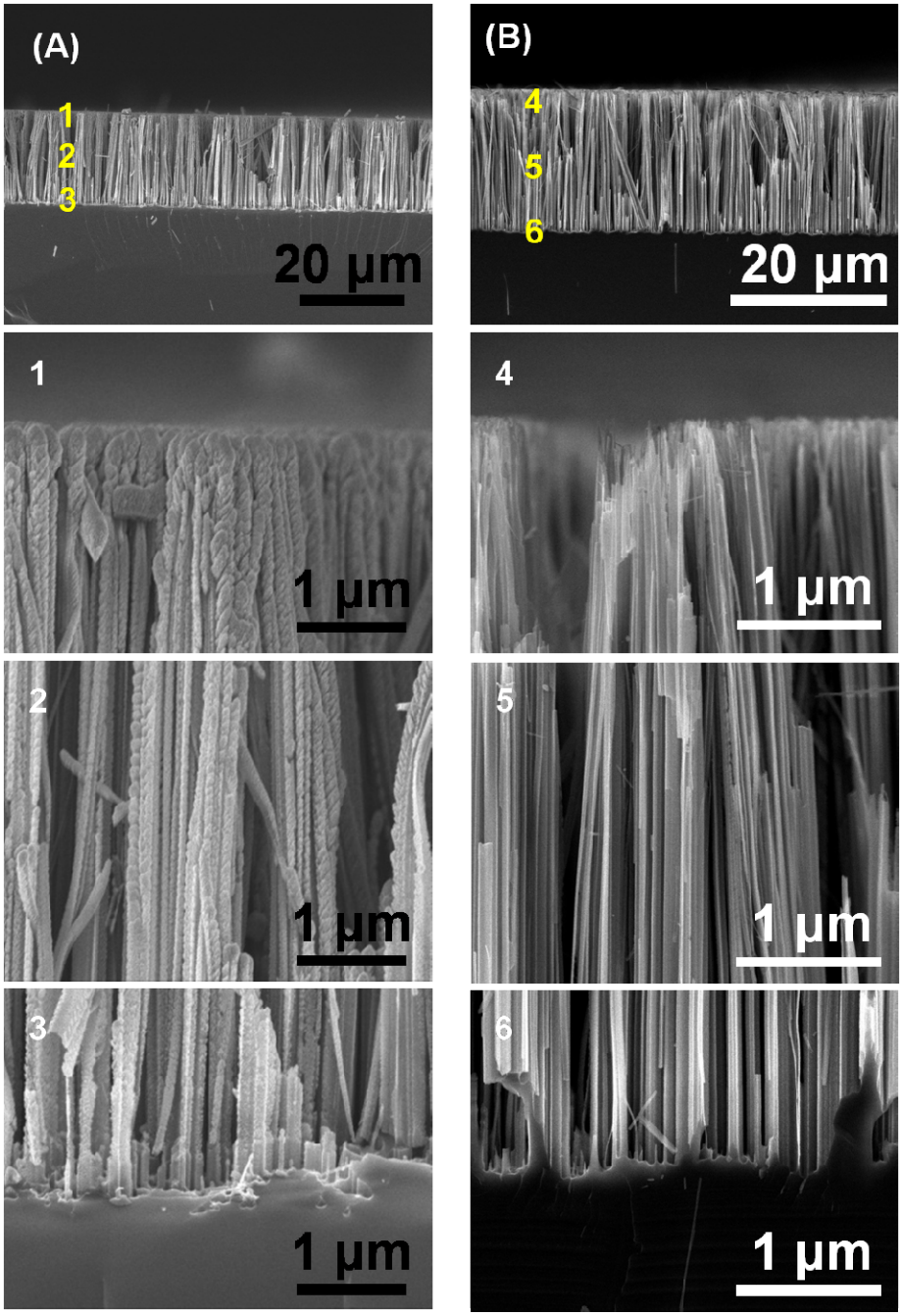

Figure S1. SEM images of rough Si NWs coated with (a) 600 nm thick Pd and (b) 7 nm thick Pd. The second (1 and 4), third (2 and 5), and fourth (3 and 6) rows show magnified images of top, middle, and bottom parts of the naowires, respectively.

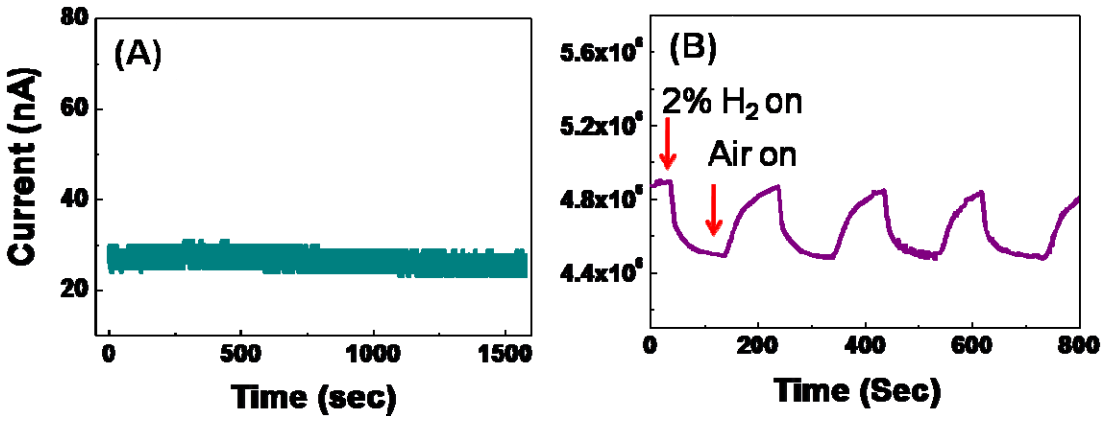

Figure S2. The real-time electrical responses of (a) pure rough Si NWs and (b) a 7 nm thick Pd film deposited on Si substrate. In (b), the points of H_2 and air injection are indicated by red arrows.

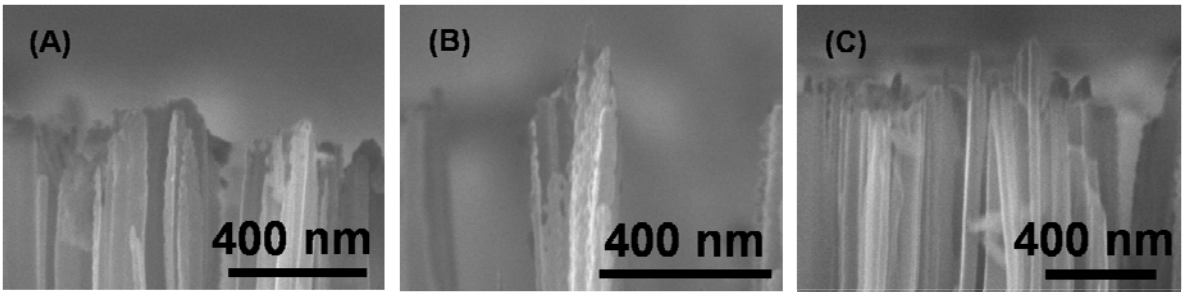

Figure S3. Changes of surface profiles of nanowires: (a) as-prepared rough Si NWs, (b) rough Si NWs coated with 7 nm thick Pd, (c) Pd-coated rough Si NWs annealed at 150 ^{o}C for 3 hours.

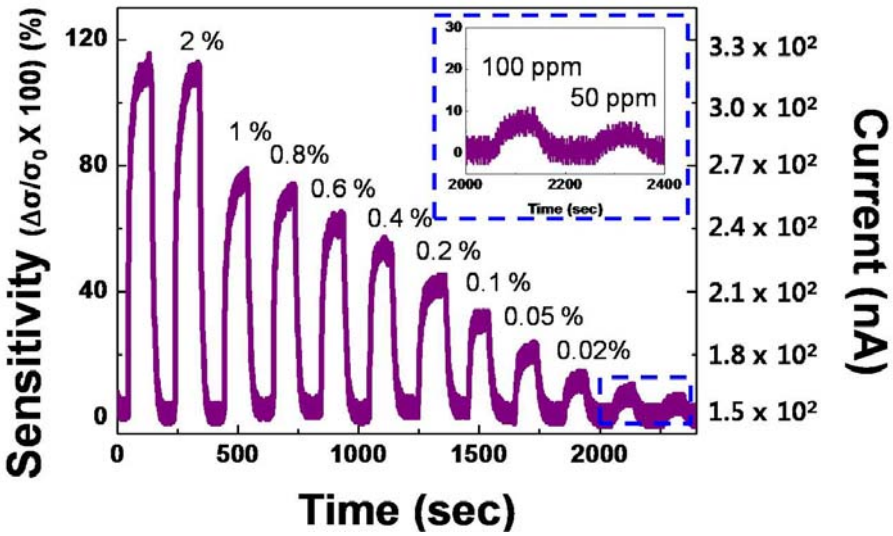

Figure S4. The real-time electrical responses of annealed Pd-coated rough Si NWs. The inset shows magnified response curves at very low H_2 concentrations.