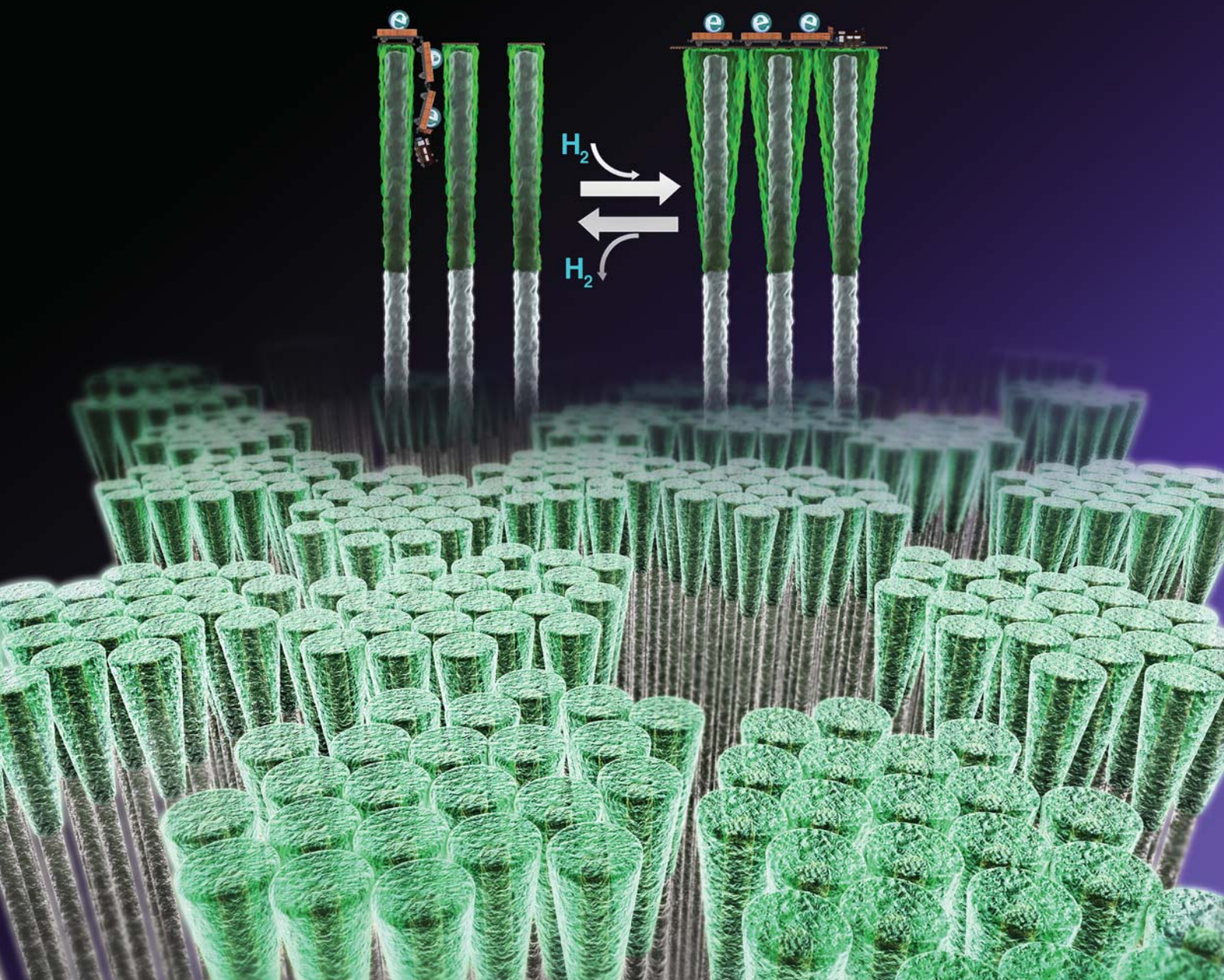


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**PAPER**

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

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

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We fabricated Pd-coated rough Si nanowires, using a combination of Si electroless etching and Pd sputtering. The semi-densely distributed, vertical-standing rough Si nanowires, which were clustered locally with inter-cluster distances of several nm to several  $\mu\text{m}$ , were selected as a basal platform. Pd was coated only on the upper part of the Si nanowires in the semi-dense configuration, and their surface profile replicated the surface morphology of Si nanowires. The Pd-coated rough Si nanowires showed good reversibility and excellent hydrogen-sensing performance in terms of sensitivity ( $>300\%$ ), response time ( $<3$  s), and detection limit ( $\sim 5$  ppm). These attributes are discussed in terms of the vertical-standing nanowire structures and the rough surface effect of the nanowires. Interestingly, the variation in sensitivity of the Pd-coated Si nanowire sensors was divided into two regimes, which appeared in the low and high hydrogen concentration ranges, respectively. A simple model is also provided to account for this unusual finding.

## 1. Introduction

Various nanomaterials and nanostructures present a promising proposal for high-performance sensing devices such as sensors based on Si nanowires.<sup>1,2</sup> The advancement of nanotechnology has also opened up new opportunities for developing gas sensors with significantly improved performance. Nanowires<sup>3–5</sup> and nanotubes<sup>6,7</sup> have been intensively investigated for this purpose, due to their nanoscale dimensions and high surface-to-volume ratio. Particularly, a variety of hydrogen gas ( $\text{H}_2$ ) sensors based on palladium (Pd) nanowires have demonstrated high sensitivities and fast response times.<sup>8–12</sup> Individual Pd nanowires have attracted special interest in pursuit of both understanding of the  $\text{H}_2$ -sensing mechanism and studying their potential as hydrogen sensors. Many groups have taken diverse approaches to prepare Pd nanowires with high quality.<sup>13–19</sup> They include electrodeposition or pressure-injection of Pd into nanochannels of porous membranes such as anodic aluminium oxide (AAO),<sup>13,14</sup> electrode patterning followed by dielectrophoresis,<sup>15,16</sup> top-down patterning from a Pd thin film using E-beam lithography.<sup>17–19</sup> However, all these methods require complex nanowire growth and nanodevice fabrication processes, which restrict their widespread use. Furthermore, the sensitivity of an individual Pd nanowire is not big enough to guarantee reliable readout signals,

demanding a means of signal amplification. Pd nanowire arrays have been proposed as a solution, where lateral Pd nanowires are randomly distributed between electrodes. However, their reproducibility needs to be further confirmed and  $\text{H}_2$  detection limits are yet to be improved. In addition, the use of Pd should be minimized in every Pd-based  $\text{H}_2$  sensors since it is rare and expensive.

Here we present Pd-coated vertical-standing rough silicon nanowires (Si NWs) as a new nanostructure for excellence in sensing  $\text{H}_2$ . They can be easily fabricated, but their performance is superb owing to the unique configuration and rough surfaces of the nanowires. A simple model is proposed to explain two distinct regimes observed in the sensitivity variation depending on  $\text{H}_2$  concentrations.

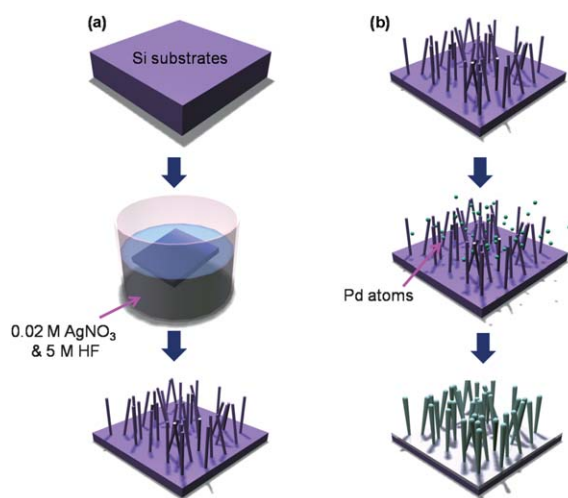
## 2. Experimental methods

Using the top-down electroless Si etching method, we achieved vertical-standing rough Si with a controllable density.<sup>20,21</sup> The schematic fabrication process is illustrated in Fig. 1(a). A 4-inch n-type (phosphorus-doped) (100) Si wafer with a thickness of  $500 \pm 25$   $\mu\text{m}$  was used. Its resistivity was 1 to 10  $\Omega$  cm. First, the wafer was cleaned in  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  solutions mixed with a volume ratio of 3 : 1 to remove organic contaminants and underwent an additional wafer cleaning process in acetone and methanol consecutively. Next, the wafer was immersed in Si etching solution consisting of 0.02 M  $\text{AgNO}_3$  and 5 M HF at room temperature. In this step,  $\text{Ag}^+$  ions dissolved in the solution are randomly deposited on the silicon surface by galvanic displacement.<sup>22</sup> The Si surface in contact with the  $\text{Ag}^+$  ions is locally oxidized to become  $\text{SiO}_2$  and then the oxide layer is etched

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**Fig. 1** Schematic pictures of fabrication processes of (a) vertical-standing rough Si NWs and (b) the subsequent Pd-coated rough Si NWs. The vertical-standing rough Si NWs are fabricated by electroless etching and then coated with a Pd thin film by sputtering.

by hydrofluoric acid. Various Si NWs with different density, length, and diameter were obtained with a control of etching time. In particular, semi-dense rough Si NWs with the height of about 20  $\mu\text{m}$  were fabricated in this work, through 70 min long Si etching. During Si etching,  $\text{Ag}^+$  ions can be attached not only on the Si substrate, but also on the pre-formed Si nanowires, which may lead partly to dendrite structures.<sup>23</sup> To remove the  $\text{Ag}^+$  ions from the surface after completion of Si etching, the substrate with nanowires on it was immersed in  $\text{HNO}_3$  (70%) solution at room temperature. Finally, it was rinsed with deionized water and dried naturally under ambient conditions.

Fig. 1(b) shows the Pd coating process to fabricate Pd-coated rough Si NWs for hydrogen sensing. A 7 nm thick Pd film was sputter-deposited on rough Si NWs under ultra-high vacuum (UHV,  $3 \times 10^{-7}$  torr). Due to the poor step coverage of the sputtering process in dense structures, the final Pd-coated Si NWs were inversely tapered. Electrodes were made simply by pasting silver on top of the Pd-coated Si NWs. A sealed chamber (250 mL in volume) was employed to measure the hydrogen-sensing performance of the Pd-coated rough Si NWs. The measurement was performed at room temperature, using air as the carrier gas. The concentration of hydrogen in air was controlled by the use of a mass flow controller (MFC). The real-time electrical response to hydrogen was measured by a current source-measurement unit (Keithley 236).

### 3. Results and discussion

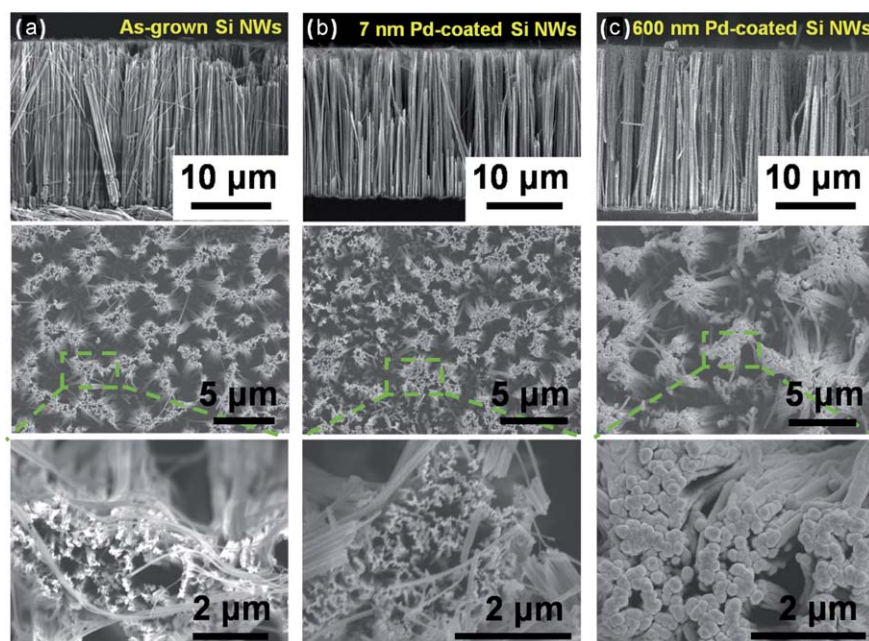
Fig. 2(a) shows scanning electron microscopy (SEM) images of semi-densely distributed vertical-standing rough Si NWs fabricated by 70 min long electroless etching. The majority of nanowires stand upright, but a small fraction of them looks slanted. The average height and diameter of the nanowires are about 20  $\mu\text{m}$  and 30–40 nm, respectively. The nanowires are moderately dense, as can be more clearly seen in middle and bottom images of Fig. 2(a). This is why we call this Si NW configuration ‘semi-densely distributed Si NWs’. From the middle image of Fig. 2(a),

it is noteworthy that many Si NWs are clustered locally. The distance between adjacent clusters ranges from several nm to several  $\mu\text{m}$ , while the inter-nanowire distance inside the clusters is estimated to be sub-nm to a few nm.

As a matter of fact, the density of Si NWs depends on the Si etching time and it generally increases with increasing the etching time. The distribution of Si NWs is also dependent on the Si etching time, since the nanowires become longer with simultaneous diameter slimming as etching is taken longer, resulting in more form instability in Si NWs fabricated through longer etching. The form instability often leads to local nanowire clustering and numerous slanted nanowires. According to our precedent experiments, the first change on the Si substrate was the formation of meandering walls when the etching time was shorter than 15 min. In this stage, the surface was etched randomly and shallowly without specific nanowires formed. Further etching started to shape rough Si NWs that were distributed loosely. When etching proceeded more (e.g., for 70 min), the nanowires become taller, thinner, and denser, but a certain degree of clustering developed as represented in Fig. 2 (a). Even longer etching (e.g., for 120 min) brought about global clustering of dense nanowires, which was not suitable for hydrogen sensing.

Fig. 2(b) displays SEM images of 7 nm thick Pd-coated rough Si NWs. The surface profiles of the Pd-coated Si NWs generally replicate the surface morphologies of the nanowires, although their diameters at top look slightly larger than those of pure Si NWs (compare middle images of Fig. 2(a) and (b)). However, it is important to examine the overall shape of the Pd-coated Si NWs along their full length, as Pd is desired to cover the Si NWs partially to avoid electrical short between two electrodes. Now that sputtering has step coverage worse than conventional chemical vapor deposition (CVD) methods, Pd is expected to hardly penetrate down to the root of Si NWs in this semi-dense configuration. To see the overall profiles of the Pd film more closely, we deposited 600 nm thick Pd on the same rough Si NWs. From Fig. 2(c), it is found that all the Pd-coated Si NWs became fat and round-shaped with the average diameter of  $\sim 200$  nm at the top. Further investigation on these nanowires revealed that the nanowires get thinner from top to bottom, resembling an inversely tapered baseball bat (see Fig. S1† for more details). This indicates that most of the Pd is deposited on the upper part of the Si NWs, minimizing the probability of current flow between the top and the bottom of the nanowires. If this is the real case, the current will flow through the Pd film deposited only around the top region of the nanowires.

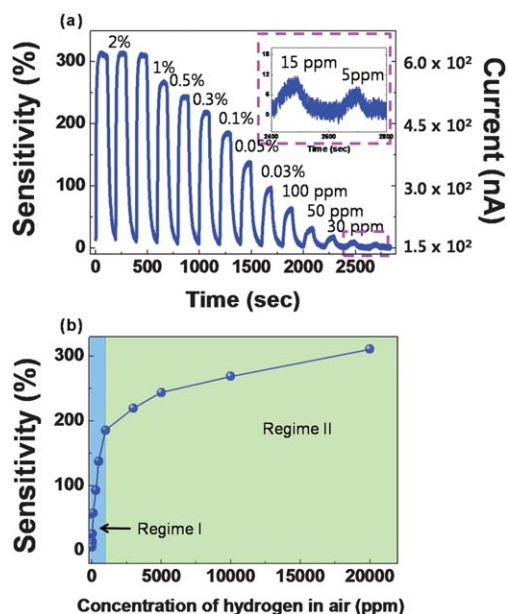
The hydrogen-sensing performance of Pd-coated rough Si NWs was tested at room temperature. Representative response curves to varying hydrogen gas ( $\text{H}_2$ ) concentrations in air are shown in Fig. 3(a). Here, the sensitivity was defined as percent conductance variation ( $\Delta\sigma$ ) upon flowing  $\text{H}_2$  to initial conductance ( $\sigma_0$ ). As can be seen from the first three cycles to 2%  $\text{H}_2$ , the hydrogen absorption and desorption processes are stable and reproducible. Surprisingly, the sensitivity surpasses 300% at 2%  $\text{H}_2$ , which is much larger than that (44% at 10%  $\text{H}_2$  in  $\text{N}_2$ ) of a single Pd nanowire.<sup>9</sup> We attribute this very high sensitivity to its semi-On–Off type operation mechanism and a bunch of vertical-standing nanowires involved in  $\text{H}_2$ -sensing. Unlike a single Pd nanowire or Pd-coated nanostructure where the resistance



**Fig. 2** Scanning electron microscopy (SEM) images of semi-densely distributed vertical-standing rough Si NWs (a) without Pd and coated with a Pd thin film of (b) 7 nm and (c) 600 nm. The top, middle, and bottom rows show cross-sectional images, top views, and magnified top views, respectively.

increases due to multiple carrier scattering on hydrogen absorption, the conductance of the initially resistive Pd-coated nanowires increases in the presence of  $H_2$  because the nearest nanowires are connected by volume expansion of the Pd film on their surface.<sup>24</sup> The vertical-standing structure helps more  $H_2$  molecules to move down to the bottom of the nanowire forest,

and numerous connections could be simultaneously made in the innumerable nanowires, mutually contributing to the enhanced conductance. The response time of the Pd-coated rough Si NWs is shorter than 3 s over the  $H_2$  concentration range of 2% to 50 ppm, when it is defined as the time to reach 30% of full conductance variation after introduction of  $H_2$ . This response time is also superior to that of a single Pd nanowire.<sup>9,12</sup> It is inferred that the rough surface profile of the Pd film replicating the surface morphology of Si NWs accelerates  $H_2$  absorption, as previously demonstrated by ion-milled Pd nanowires.<sup>25</sup> The limit of detecting  $H_2$  is 5 ppm in this work, as shown in the inset of Fig. 3(a). The sensitivity is approximately 6% at this low  $H_2$  concentration. This detection limit is the lowest level ever reported to our knowledge, which can be detected reliably in air. It may be ascribed to the closely placed vertical-standing nanowire structure<sup>26</sup> that can allow local bridges to be formed even by infinitesimal volume expansion of the Pd film.

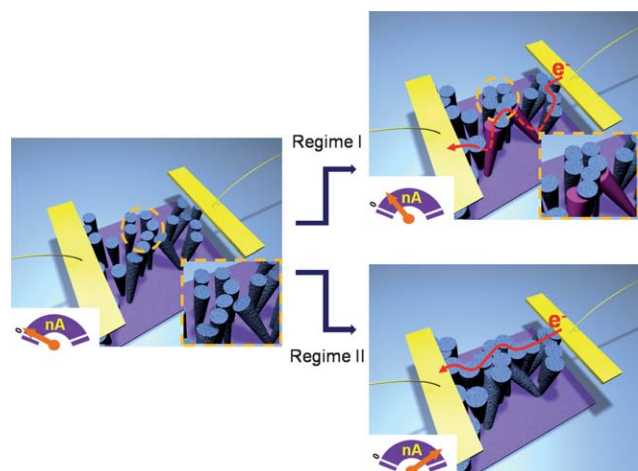


**Fig. 3** (a) The real-time electrical response curves of semi-densely distributed vertical-standing rough Si NWs coated with a 7 nm thick Pd film to varying  $H_2$  concentrations in air at room temperature. The inset shows clear response behaviours even at very low  $H_2$  concentrations down to 5 ppm. (b) A plot of sensitivity vs.  $H_2$  concentrations revealing two regimes with different rates of sensitivity change.

In Fig. 3(a), the sensitivity is in general scalable depending on the  $H_2$  concentration in air. To make it clear, the sensitivity vs.  $H_2$  concentration is plotted in Fig. 3(b). Although the sensitivity generally decreases as the  $H_2$  concentration decreases, the graph is divided into two regimes around 1000 ppm of  $H_2$  according to the rate of sensitivity change. The sensitivity is overall high and changes slowly in regime II (high  $H_2$  concentrations), whereas it rapidly changes with varying  $H_2$  concentrations in regime I (low  $H_2$  concentrations). This is in contrast with the normal sensitivity variation trend originating from the intrinsic  $\alpha$  to  $\beta$  phase transition of the Pd film, for which the sensitivity changes slowly at low  $H_2$  concentrations and then abruptly increases around the phase transition point.<sup>27</sup> Moreover, the cusp point (1000 ppm  $H_2$ ) appears far lower than the  $H_2$  concentration ( $\sim 1.5\%$ ) for the intrinsic phase transition in the Pd film.<sup>27,28</sup> In addition, significant structural deformations that might be a clue for the  $\alpha$  to  $\beta$  phase transition were not observed in our Pd films coated on Si

NWs. The inhibition of structural deformations could be explained by synergistic contributions from reduction of the Pd film thickness (7 nm) and improved adhesion between the Pd film and Si NW afforded by rough interface profile. For these reasons, we believe that structural deformations initiated by the  $\alpha$  to  $\beta$  phase transition in the Pd film are unlikely to produce the cusp in the sensitivity variation trend. Instead, the configuration of Pd-coated Si NWs is more likely to be responsible for this observation.

To account for this interesting phenomenon, we propose a simple model here, as schematically presented in Fig. 4. As explained above, the Pd-coated rough Si NWs are comprised of many nanowire clusters with variable distances between them. The inter-cluster distance is on average larger than the average distance between individual nanowires inside the clusters, as shown in the left panel of Fig. 4. In the high  $H_2$  concentration range (regime II), current paths are activated by contacting neighboring clusters in addition to perfect contact formation between almost all nanowires inside each cluster. This situation leads to high current conduction as represented by the bottom-right panel of Fig. 4. Provided that low  $H_2$  concentration range (regime I) is considered, it is hard to connect neighboring clusters by small expansion of the Pd film. Just intra-cluster nanowires spaced by sub-nm can be contacted to each other, corresponding to the amount of Pd volume expansion caused by  $H_2$  absorption. Because the neighboring clusters are bridged by slanted nanowires in this case, conductance increase is not that much, as indicated by the top-right panel of Fig. 4. Although the overall sensitivity is larger in regime II than in regime I, the sensitivity change per unit change in the  $H_2$  concentration is more pronounced in regime I. This may be because the entire current conduction between electrodes is limited by gaps between relatively high-conductive



**Fig. 4** A proposed model of the hydrogen-sensing mechanism. The left panel represents the initial Pd-coated rough Si NWs consisting of several clusters. The inset of the left panel shows a magnified distribution of Si NWs inside a cluster. The top-right panel illustrates nanowire contacts inside clusters with gaps between neighboring clusters. In this case, the current flows through slanted nanowires between clusters. The inset of the top-right panel is a magnified picture of contacted distribution of Si NWs inside a cluster. The bottom-right panel illustrates the formation of current paths between neighboring clusters by large volume expansion of the Pd film caused by absorption of high concentrations of  $H_2$ .

clusters and nanowires situated in the gaps are sensitively activated as conduction bridges in response to a change in  $H_2$  concentration. For a simple calculation, assuming 1000 circular Pd-coated Si NWs are included in each of two adjacent circular clusters with 100 nanowires arranged along the center line each, about 1% lattice expansion of the Pd film is required to connect the two clusters, when taking the spacing between the two clusters and the Pd film thickness deposited at the top of Si NWs as 20 and 10 nm, respectively. This magnitude of Pd expansion cannot be reached at  $H_2$  concentrations below 1000 ppm.

#### 4. Summary

We fabricated vertical-standing Pd-coated rough Si NWs, using electroless etching followed by sputtering. Their configuration was controlled mainly by controlling the etching time, and the semi-dense Si NWs that include many nanowire clusters placed non-uniformly were prepared by 70 min long etching. The Pd-coated rough Si NWs exhibited the surface profile replicating the surface morphology of the rough Si NWs and was inversely tapered overall, employing a 7 nm thick Pd film. Hydrogen-sensing performance of the nanowires appeared to be excellent in terms of the reproducibility of response, sensitivity, response time, and detection limit. It was explained by a combination of vertical-standing nanowire structure, unique semi-dense configuration, and rough nanowire surface. A simple model was also proposed to account for an interesting cusp in the sensitivity variation trend. The vertical-standing Pd-coated rough Si NWs may provide a promising opportunity for achieving high-performance hydrogen sensors.

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