Electronic Supporting Information (ESI†)

Ultrasensitive detection of low-ppm H_2S gases based on palladium-doped porous silicon sensors

Nu Si A Eom [a]†, Hong-Baek Cho[b]†, Hyo-Ryoung Lim[b], Tea-Yeon Hwang[b], Yoseb Song[b], and Yong-Ho Choa[b]*

[a] Electrochemistry Department, Korea Institute of Materials Science, Changwon, 51508, Republic of Korea

[b] Department of Fusion Chemical Engineering, Hanyang University, Ansan, 15588, Republic of Korea

† These authors contributed equally to this work.

Corresponding author: Yong-Ho Choa
Tel.: +82 11 9629 7446; Fax: + 82 31 418 6490
E-mail address: choa15@hanyang.ac.kr

Experimental details for the calculation of Pd content (%) based on H_2 chemisorption data

The dispersion and surface area were very small because the metal dispersion and surface area data from H_2 chemisorption strongly depend on the effect of weight. The Pd content (%) was calculated based on the following equation:

$$Pd\ weight\ = \rho\left[{}^{g}/_{cm^3}\right] \times m\ [cm^2] \times n\ [nm] \qquad \text{--} \quad 1)$$

$$= 12.023\ {}^{g}/_{cm^3} \times 1\ cm^2 \times 3\ nm\ (1\ nm = 10^{-7}\ cm)$$

$$= 12.023\ {}^{g}/_{cm^3} \times 1\ cm^2 \times 3 \times 10^{-7}\ cm)$$

$$= 3.61 \times 10^{-6} g$$

where ρ is the density of Pd (12.023 g/cm³), m is the silicon surface area for palladium deposition, and n is the average Pd metal thickness from E-beam evaporation, which is estimated based on the E-beam evaporation conditions (UEE, ULTECH, Korea).

$$Si\ weight\ = \rho\left[{}^{g}/_{cm^3}\right] \times p\ [cm^2] \times q\ [nm] \qquad \text{--} \quad 2)$$

$$= 2.23\ {}^{g}/_{cm^3} \times 1\ cm^2 \times 300\ \mu m\ (1\ \mu m\ \times 10^{-4} cm)$$

$$= 2.23\ {}^{g}/_{cm^3} \times 1\ cm^2 \times 300\ \times 10^{-4} cm$$

$= 6.99 \times 10^{-2} g$

where ρ is the density of Si (ρ: 2.33 g/cm^3), p is the silicon surface area, and q is the thickness of the silicon wafer (300 μm)

Pd weight percentage:

$$= \frac{3.61 \times 10^{-6}\text{g}}{3.61 \times 10^{-6}\text{g} + 6.99 \times 10^{-2}\text{g}} \times 100\%$$

= 0.00516 %

According to the above equation, the weight percentage of 3-nm Pd on a 300 μm porous layer silicon is 0.00516%. Considering 0.00516 wt% Pd on porous silicon, the dispersion of Pd metal on a porous layer with a thickness of 15 μm or 90 μm increased from 0.0071% to 0.012%, with the corresponding metal surface area increasing from 0.0317 m^2/g to 0.0533 m^2/g. Although an identical Pd content was utilized for deposition, the number of Pd metal deposition sites was expected to increase with the increased diameter of the porous layer up to an electrochemical etching time of 60 min because the surface area of the *p*-Si increased. Consequently, the enhanced dispersion and surface area of the Pd catalyst led to an increase in chemisorption sites, resulting in the enhancement of sensing performance.

Figure Captions

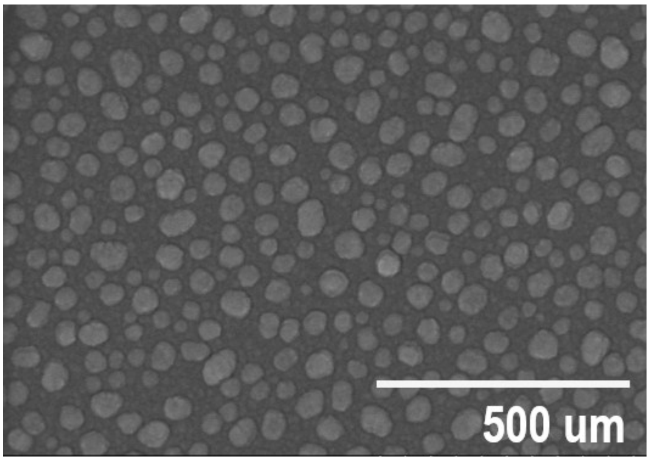

Figure S1. SEM image of 30-60 nm Pt metal particles formed on the Si substrate after deposition and heat treatment at 650°C.

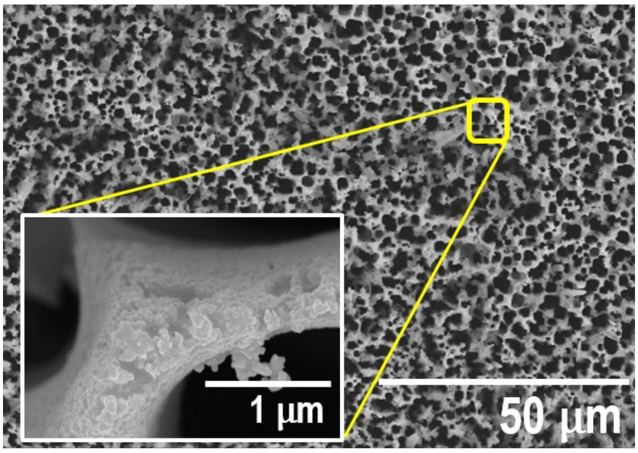

Figure S2. SEM image of the surface morphology of the porosity generated on the pristine Si substrate.

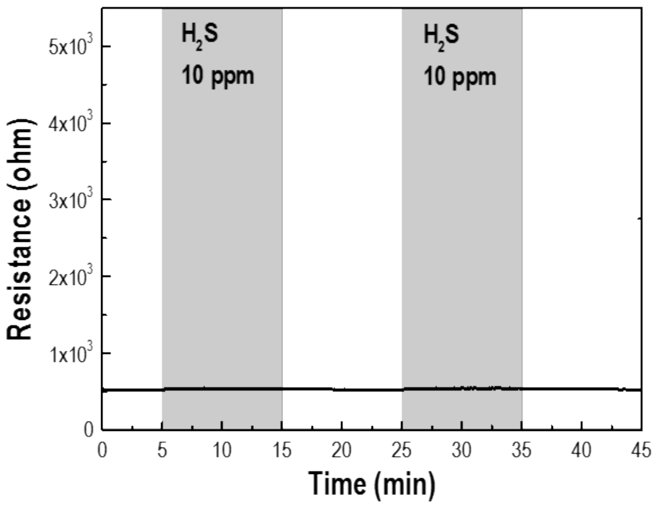

Figure S3. Sensing curve of the non-doped 90-µm-thick porous Si wafer substrate under exposure to 10 ppm of H_2S gas at room temperature.

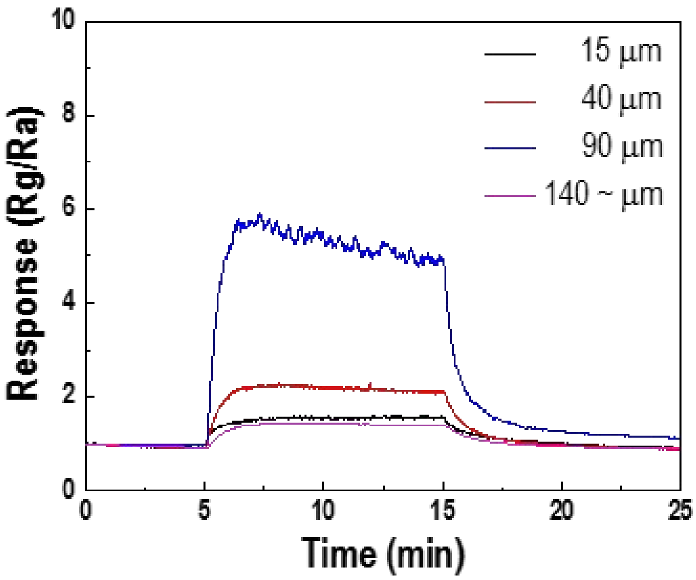

Figure S4. Comparison of the gas response (Rg/Ra) of Pd/p-Si sensors as a function of etching time under exposure to 10 ppm H_2S.

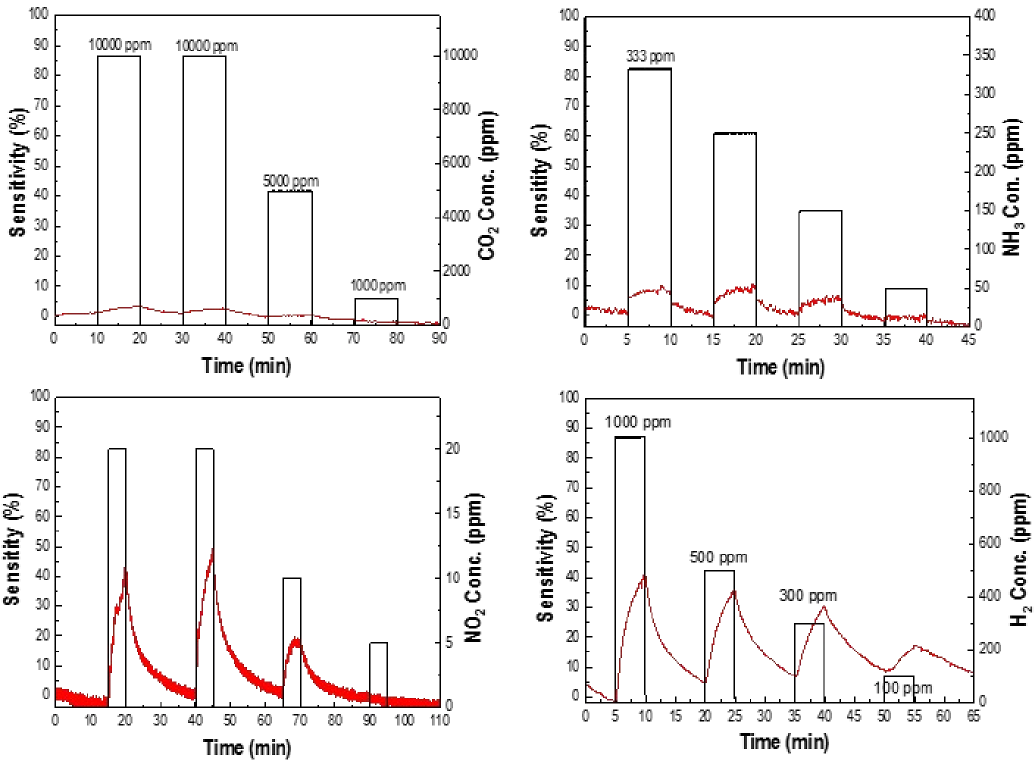

Figure S5. Selectivity of the Pd/*p*-Si gas sensor of 90 µm thickness for various detecting gases at room temperature.

Table S1. Metal doped porous silicon or semiconductor gas sensors for H_2S gas detection

Sensor	Concentration	Temperature	Response	Recovery	Reference

materials	(ppm)	(°C)	time	Time	
Au/PS/Si	45	RT	60 s	~ 180 s	Jpn. J. Appl. Phys. **47** (2008) 8204
Pd-gate MOS transistor	50	150	~ 120 s	180 s ~	Sens. Actuators, **15** (1988) 85
Au sensitized ZnO rods	3	RT	10 min	13 min	Abbreviated Title J. Alloys Compd. **628** (2015) 222
Cu_2O/SnO_2 multi-layer	50	RT	160-180 s	240-500 s	Sci. Rep., **3** (2013) 1250
This paper	**10**	**RT**	**65**	**165**	**In this paper**

Table S2. Metal doped porous silicon sensors for H_2 gas detection

Sensor materials	Concertation (ppm)	Reference
Au modified PS	15 ppm H_2	Prog. Nat. Sci.: Mater. Int. **25** (2015) 101
Pd-Ag/Pd:ZnO/Pd:PS/Si/Al	1% H_2	Sens. Actuators, B **147** (2010) 128
Graphene doped porous silicon	100 ppm H_2	Sensors **17** (2017) 2750