## Near Single Crystalline TiO<sub>2</sub> Nanohelices Array: Enhanced Gas Sensing Performances and its Application as Monolithically Integrated Electronic Noses

Sunyong Hwang,<sup>*a*</sup> Hyunah Kwon,<sup>*a*</sup> Sameer Chhajed,<sup>*a*</sup> Ji Won Byon,<sup>*b*</sup> Jeong Min Baik,<sup>*b*</sup> Jiseong Im,<sup>*a*</sup> Sang Ho Oh,<sup>*a*</sup> Ho Won Jang,<sup>*c*</sup> Seok Jin Yoon<sup>*d*</sup> and Jong Kyu Kim\*<sup>*a*</sup>

\*E-mail: kimjk@postech.ac.kr

<sup>a</sup> Department of Materials Science and Engineering, POSTECH, Pohang 790-784, Republic of Korea.

<sup>b</sup> School of Mechanical and Advanced Materials Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-805, Republic of Korea

<sup>c</sup> Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul 151-742, Republic of Korea.

<sup>d</sup> Electronic Materials Center, Korea Institute of Science and Technology (KIST), Seoul 136-791, Republic of Korea.

## This supplementary information contains figures with the following captions:

**Fig. S1** (a) The bird's eye view SEM image of the  $TiO_2$  nanohelix gas sensor. A small part of the sensor indicated by the red circle is the area where FIB milling was performed. (b) Magnified image of the red-circled part in (a). (c) Cross-section view SEM image of the device showing the nano-porous  $TiO_2$  nanohelices array sandwiched by the top and the bottom electrodes.

Fig. S2 (a) Refractive indices of  $TiO_2$  thin film and  $TiO_2$  nanohelices array measured by an ellipsometer. (b) Simple model used to estimate the relative increase in surface area for the nanohelices array.



**Fig. S1** (a) The bird's eye view SEM image of the TiO<sub>2</sub> nanohelix gas sensor. A small part of the sensor indicated by the red circle is the area where FIB milling was performed. (b) Magnified image of the red-circled part in (a). (c) Cross-section view SEM image of the device showing the nano-porous TiO<sub>2</sub> nanohelices array sandwiched by the top and the bottom electrodes.

Fig. S1(a) shows a bird's eye view SEM image of the fabricated  $TiO_2$  nanohelix gas sensor. In order to check if the array of  $TiO_2$  nanohelices is properly fabricated between the top-and-bottom electrodes, a small part of the active region of the device, as indicated by red circle, was exposed by using focused ion beam (FIB) etching. Fig. S1(b)-(c) show magnified SEM images of the FIB-etched region. As shown in Fig. S1(c), the active layer seems very porous, but it doesn't look like an array of helices because the FIB etching made the 2dimensional cross-section of the active region from the 3-dimensional helix structure, possibly with some ion-beam damages. However, in the cleaved cross-section of the device, as shown Fig. 1(g), nanohelices array is clearly seen, indicating that an ordered array of  $TiO_2$ nanohelices was fabricated successfully.



**Fig. S2** (a) Refractive indices of  $TiO_2$  thin film and  $TiO_2$  nanohelices array measured by an ellipsometer. (b) Simple model used to estimate the relative increase in surface area for the nanohelices array.

Refractive indices of TiO<sub>2</sub> thin film and nanohelices array were measured by an ellipsometer using the Cauchy model and the effective medium approximation (EMA) (Fig. S2(a)). The refractive index of the dense TiO<sub>2</sub> thin film deposited by the electron-beam evaporator with the normal deposition angle is 2.18, and that of the TiO<sub>2</sub> helices array fabricated rotating OAD is 1.57 at 550 nm. By using the linear EMA, the porosity of the TiO<sub>2</sub> nanohelices array is estimated to be 51.9 %. In order to estimate the increase in the surface area of the nanohelices array, a simple model is set-up as shown in Fig. S2(b). For simplicity, vertical nanorods with the diameter of 22 nm, and the length of 400 nm are assumed to be uniformly distributed in the square lattice. The porosity *P*, which was estimated to be ~ 52% experimentally, can be represented as  $P = \pi r^2/L^2$ , where L is the length of the one square lattice unit cell which can be estimated to be L = 27.1 nm.

Next, let us consider a thin film with the thickness of 400 nm and top surface area of 100  $\mu m$   $\times$  100  $\mu m.$ 

Then,

(i) Surface area of thin film = top surface area + sidewall area ~  $10^4 \mu m^2$ 

Considering the nanorod array within the same volume of the thin film,

(ii) Surface area of nanorod array = top surface area of nanorods array + sidewall area of nanorods array = number of nanorods in the array × top surface area of a nanorod + number of nanorods in the array × sidewall area of each nanorod =  $(100 \ \mu\text{m} / 27.1 \ \text{nm})^2 \times \pi \times 11^2 \ \text{nm}^2 + (100 \ \mu\text{m} / 27.1 \ \text{nm})^2 \times 2\pi \times 11 \ \text{nm} \times 400$ nm =  $3.81 \times 10^5 \ \mu\text{m}^2$  Therefore, the increase in surface area for the nanohelices array compared to the thin film is estimated to be  $3.81 \times 10^{5}/10^{4} = 38.1$