

## Supporting information for

# **“A novel reaction model for the electrical conductivity of ultra-thin TiO<sub>2</sub> films in H<sub>2</sub>”**

Chi Lu <sup>a</sup>, Zhi Chen <sup>a</sup> and Ping Yu <sup>b</sup>

<sup>a</sup> *Department of Electrical and Computer Engineering and Center for Nanoscale Science and Engineering, University of Kentucky, Lexington, KY 40506, USA*

<sup>b</sup> *Metabolism Branch, National Cancer Institute, National Institutes of Health, Bethesda, MD 20892, USA*

### **Experimental details:**

**Two-step anodisation of the evaporated aluminum films:** A 0.3 M oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) solution was prepared by dissolving 19 g oxalic acid dihydrate (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) crystal powder in 500 ml de-ionized (DI) water. The anodisation was carried out in this prepared solution at room temperature. The sample, which was a commercial (100) silicon wafer coated with a 2.2 μm-thick aluminum (Al) layer on the polished side, was used as the anode and a platinum (Pt) plate served as the cathode (counter electrode). A constant bias voltage of 40 V was applied between the two electrodes during the anodisation by a power supply and a galvanometer was connected in the loop to monitor the current. The overall setup is shown in Fig. S1.

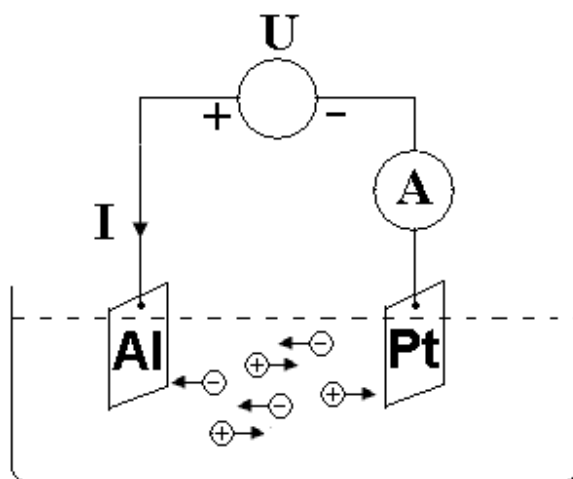
After anodisation for 5 min (first-step anodisation), the sample was removed from the anodisation setup and then immersed in a mixed solution of chromic acid (1.8 wt%) and phosphoric acid (6 wt%) at 65~70°C for 2-5 min. Next, the sample was anodized again in the same anodisation setup (second-step anodisation), until the shiny Al metal layer was completely converted into transparent aluminum oxide ( $\text{Al}_2\text{O}_3$ ). The loop current dropped to almost zero at the end of the second-step anodisation. Fig. S2 is a diagram for the two-step anodisation.

Once the anodisation was completed, the sample was rinsed thoroughly in DI water and then immersed in a 0.6 M phosphoric acid solution for 30 min at room temperature for pore widening. Finally, the sample was rinsed thoroughly in DI water again.

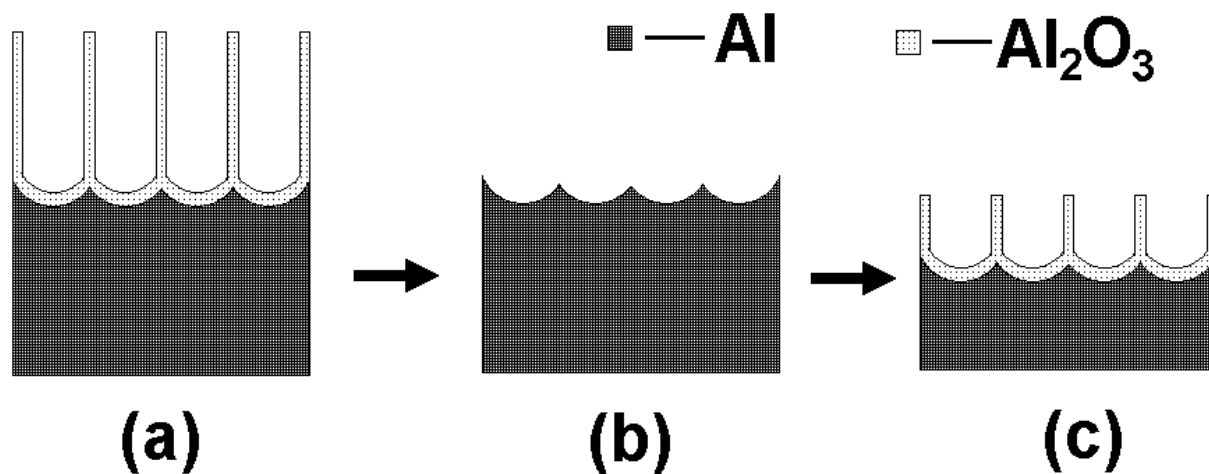
**Preparation of the ultra-thin  $\text{TiO}_2$  films and Pt electrodes:** A approximately 9 nm-thick titanium (Ti) metal layer was deposited on the anodic aluminum oxide (AAO) film prepared in the previous section, as well as on a commercial ceramic plate, through electron beam evaporation under high vacuum (pressure: around  $3 \times 10^{-6}$  torr before the evaporation and around  $2 \times 10^{-5}$  torr during the evaporation; evaporation rate: 0.3~1 Å/s). The Ti-coated samples (Ti/AAO/wafer and Ti/ceramic) were sintered at 600°C for 6 h in synthetic air with a flow rate of 1000 ml/min. Finally, two interdigital platinum electrodes with a spacing of 25  $\mu\text{m}$  were fabricated on both of the sintered samples by photolithography and electron beam evaporation. The thickness of the platinum electrodes was about 60 nm. Fig. S3 shows the entire fabrication process flows for both devices. However, both of the substrate surfaces (AAO and ceramic) are so rough that neither profilometry nor ellipsometry could be able to precisely measure the thickness of the titanium dioxide ( $\text{TiO}_2$ ) resulting from the 600°C oxidation and sintering.

Besides, the oxidation aggravates the irregularity of the originally deposited Ti layer. Therefore, in the present study, the best way we could do is to use the original Ti thickness recorded by the crystal monitor incorporated in the electron beam evaporator to represent the post-oxidation TiO<sub>2</sub> thickness.

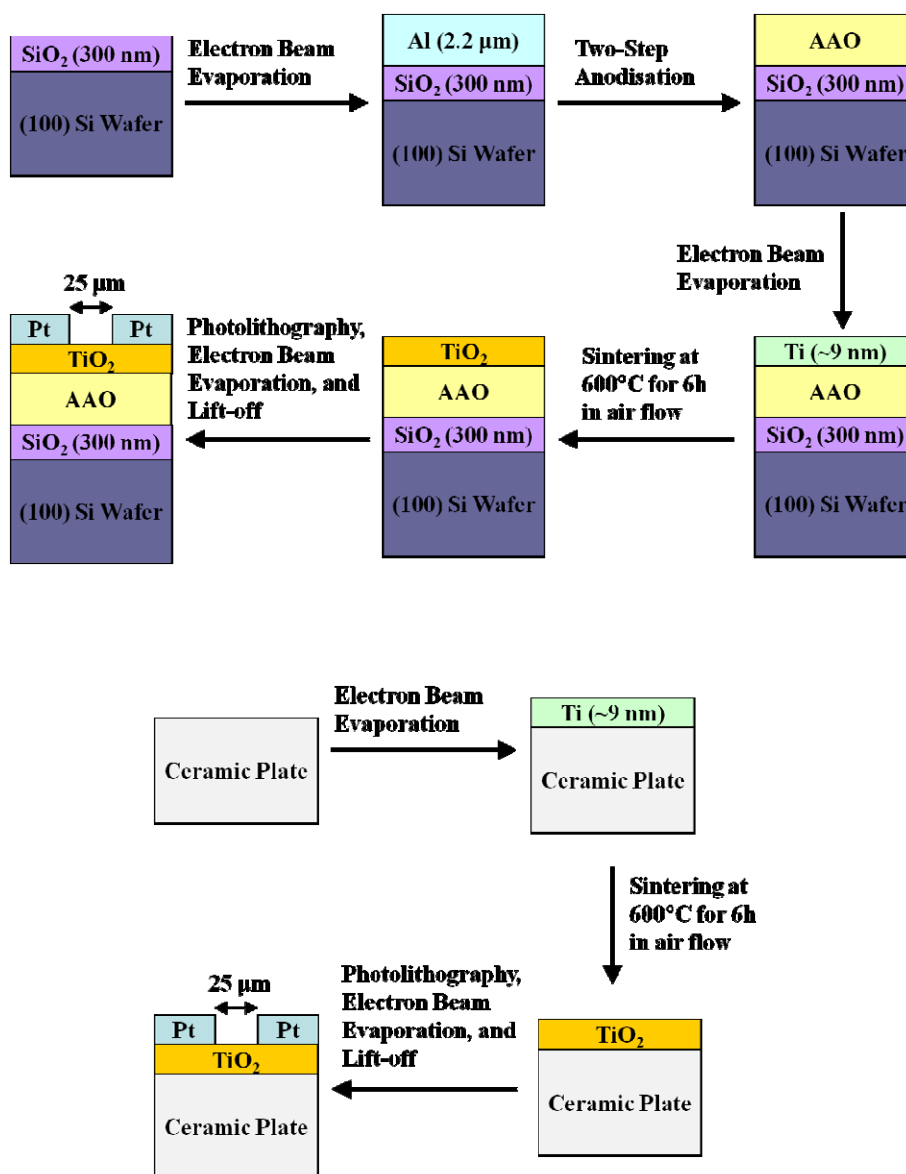
**Gas sensing measurements:** The device (TiO<sub>2</sub>/AAO/water or TiO<sub>2</sub>/ceramic) was placed in a quartz tube in a furnace and the furnace temperature was stabilized at 500°C. Resistance measurements at different hydrogen concentration levels (0, 5, 10, 20, 50, 100, 200 and 500 ppm) were performed with N<sub>2</sub> as the carrier gas. The H<sub>2</sub> concentration was controlled by mixing a premixed 1000 ppm N<sub>2</sub>-diluted H<sub>2</sub> gas and a pure N<sub>2</sub> gas, while the total gas flow rate in the quartz tube was maintained constant (1000 ml/min). I-V scans were performed by a power supply and a galvanometer. Within the range of the applied voltage (-1 to +1 V; step: 0.1 V), the current was always directly proportional to the voltage, in all H<sub>2</sub> concentrations for both devices. Therefore the devices were identified as resistors. The conductance was measured by a digital multimeter. In pure nitrogen ambient at 500°C, the conductance of the TiO<sub>2</sub> on AAO (1.4 μS) is about four times of the TiO<sub>2</sub> on ceramic plate (0.33 μS). This can be attributed to the much higher roughness of the AAO surface that collects substantially more Ti during the evaporation. Although a larger amount of Ti accumulates on the AAO, the resulting difference in the TiO<sub>2</sub> conductance is still within a half-order (less than 5 times).



**Fig. S1** Scheme of the anodisation setup. The symbols in the solution represent the moving cations and anions. “I” represents the electric current and “U” is the applied voltage or the power supply. The galvanometer is symbolized by the “A” in the circle.



**Fig. S2** Scheme of the two-step anodisation. (a) At the end of the first-step anodisation. (b) After immersing in the chromic-phosphoric acid solution. The Al<sub>2</sub>O<sub>3</sub> formed in the first-step anodisation is totally etched away. (c) During the second-step anodisation. New AAO pores grow from the texture resulting from the first-step anodisation at the surface of the Al metal.



**Fig. S3** Process flows of the device fabrication for the TiO<sub>2</sub>/AAO/wafer (top) and the TiO<sub>2</sub>/ceramic plate (bottom).