Facile Fabrication of TiO$_2$ Nanorod Arrays for Gas Sensing using Double-Layered Anodic Oxidation Method

Hsiao-Wei Lin, Yung-Huang Chang, and Chih Chen$^z$

Department of Materials Science and Engineering, National Chiao-Tung University, Hsinchu, 30010 Taiwan

Self-organized anodic titanium dioxide nanorod arrays were fabricated using a two-stage anodization method from superimposed Ti-Al layers deposited on quartz substrates. The morphology of nanorods could be controlled by the anodizing conditions of the aluminum (first stage) and the titanium layer (second stage). The first stage of anodization process controls the diameter and density of nanorods and the second stage of anodization controls the height of nanorods. Therefore, we could fabricate nanorod arrays with desired aspect ratio and density under specific anodizing conditions. Furthermore, we used TiO$_2$ nanorod arrays as the field ionization anode of a gas sensor, and the morphology of nanorods has shown to have a high correlation with the working voltage of gas sensing. The TiO$_2$ nanorods possess good selectivity and low working voltage under different atmosphere and their working electric field is lower than gas sensing using carbon nanotubes and ZnO nanowires as the anode.

Results and Discussion

In order to confirm that nanorods fabricated by this method are TiO$_2$, XPS was used for the analysis of chemical composition. All spectra were referenced to C 1s at 284.5 eV, Figure 2 shows the Ti 2p core-level spectra as a function of sputtering time for the anodized Ti-Al bilayers. From the figure, the measured spectrum consists of layer by a thermal evaporation coater to form a Ti-Al double-layered specimen. The use of quartz wafer was necessary to provide a flat substrate surface to support the Ti-Al bilayer, for easy preparation of film fractures for scanning electron microscopy observations and to avoid ambiguity in interpreting X-ray photoelectron spectrometer results. The wafer with the superimposed metal layers was cut into pieces of ca. 2 × 2.5 cm which were then individually anodized in an in-house designed equipment. The sample was placed vertically on the equipment and an o-ring was set between the sample and the equipment so that only a surface area of 2.24 cm$^2$ was in contact with the electrolyte of 0.3 M oxalic acid. A Keithley 2400 sourcemeter controlled by computer software was used as the anodizing power supply and the recorder of current density characteristics.

In order to control the morphology of the TiO$_2$ nanorods, a two-step anodization process was used in this study.$^{26,29}$ In the first stage the aluminum was anodized at a voltage $V_{\text{Al}}$. After the current density was dropped down to 1 mA cm$^{-2}$ indicating the completion of the anodization of the aluminum layer, the process was either interrupted or the voltage was increased to $V_T$ for further anodization of the titanium through the AAO mask. Fig. 1 shows the behavior of current density vs time for the two-stage anodization of the Al/Ti/quartz sample in 0.3 M oxalic acid electrolyte under room temperature. The applied voltage of the first stage (part I, Fig. 1a) and the second stage (part II, Fig. 1a) of anodization were controlled by a computer program to produce different densities, diameters and aspect ratios of TiO$_2$ nanorod arrays, as shown in Table I. After the two-step anodization process, the overlying AAO film was selectively removed by wet chemical etching at 60°C in a mixed solution of phosphoric and chromic acid for 40 min. This approach produces self-aligned TiO$_2$ nanorod arrays with controlled morphology on the quartz substrate. The morphologies and microstructures of the samples were characterized with a JEOI JSM-6500F field-emission scanning electron microscope (FESEM). The chemical composition and bonding states in the anodic films were examined by XPS analysis carried out in an ESCA PHI 1600 system equipped with an Al K$\alpha$ monochromatized X-ray beam and a charge neutralizer. Figure 1b shows the setup of a field ionization gas sensor consisting of two electrodes, our sample as the anode and indium tin oxide (ITO) as the cathode. The gap between the anode and the cathode was fixed at 579 μm. The pressure in the chamber was maintained at 10$^{-3}$ Pa.$^{31}$

Gas sensors are operated based on a variety of mechanisms. Basically, they are classified into two types: chemical types operated by adsorption and physical types managed by gas ionization. Chemical types mainly detect the electrical response of the gas molecules adsorbed by an active layer in the gas sensor to identify the concentration and composition of gases. However, they usually require a high working temperature, a long pre-heating time and a large surface area. They also encounter high power consumption problem and are not able to detect inert gases.$^{1-5}$ Physical types usually use ionization fingerprint properties of gases for the identification process, and carbon nanotube (CNT) arrays are mostly incorporated into this kind of device because of their low operating voltage. However, the drawback is the degradation problem of CNT due to oxygen contained in air.$^{6-10}$

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two doublet peaks, 2p_{1/2} and 2p_{3/2}. In the beginning of sputtering, the positions of the main peaks remained unchanged, corresponding to the Ti^{4+} state at 458.9 and 464.6 eV,\textsuperscript{33, 34} which means the main composition of the nanorods was TiO_2 and no metallic titanium was remained on the surface of the nanorods. After sputtering for 400 s, a shoulder appeared at the low energy edge which then developed into an additional doublet peak in the spectra, corresponding to the metallic Ti^{0} state at 454 and 460 eV.\textsuperscript{33, 34} It indicates that some un-anodized Ti metal still remained underneath the TiO_2 nanorods. Figure 3 shows the O 1s core level spectra as a function of sputtering time for the sample. The measured spectrum O 1s in the as-fabricated nanorods consisted of a peak at 531.7 eV. After 200 s sputtering, it shifted to 530.6 eV and then gradually decreased with the sputtering time. The binding energy of O-Al and O-Ti are 531.8 and 530.4 eV, respectively.\textsuperscript{35} This indicates that the peak shifting may be due to the contribution of oxygen bond in alumina and the O 1s peak was only related to the oxygen bond in titanium dioxide after sputtering. It revealed that the surface of titanium nanorods contain small amount of alumina, as confirmed again by the Al 2p core level spectra shown in Figure 4. The measured spectrum of the as-fabricated nanorods consisted of a peak at 74.5 eV, which was attributed to oxidized aluminum.\textsuperscript{24}

Table 1. The voltages for the first-stage and the second-stage anodization of the Ti-Al bilayers.

<table>
<thead>
<tr>
<th>Type</th>
<th>Different $V_{AI}$ with $V_{Ti}$ fixed</th>
<th>Different $V_{Ti}$ with $V_{AI}$ fixed</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{AI}$</td>
<td>10 V  20 V  40 V  60 V  40 V  40 V  40 V  40 V</td>
<td></td>
</tr>
<tr>
<td>$V_{Ti}$</td>
<td>100 V  100 V  100 V  100 V  100 V  60 V  80 V  100 V</td>
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Figure 2. XPS Ti 2p peaks as a function of sputtering time for the nanorod arrays fabricated from the superimposed Ti-Al layers which had been anodized in a 0.3 M oxalic acid after removing the overlaying AAO mask.

Figure 3. XPS O 1s peaks as a function of sputtering time in the fabricated nanorod arrays which had been anodized in a 0.3 M oxalic acid after the removal of the overlaying AAO mask.

Figure 4. XPS Al 2p peaks as a function of sputtering time for the fabricated nanorod arrays in a 0.3 M oxalic acid after the removal of the overlaying AAO mask.
hand, their average diameter increases with the increase of anodization voltage $V_{Al}$. The results indicate that $V_{Al}$ is the dominant factor affecting the density and the diameter of TiO$_2$ nanorods. In general, the diameter of nanorods is highly related to the size of AAO pores. However, the actual diameter of nanorods is slightly larger than that of the AAO pores under the same anodizing voltage because the walls of AAO pores are contaminated with protons, defects or some electrolyte species resulting in lower ion resistivity.  

The growth heights of nanorods under four different growth conditions performed in our study are approximately the same. Figure 6a to 6d show the cross-sectional SEM images for fabricated TiO$_2$ nanorods under different anodizing conditions performed in our laboratory. Figure 6 shows the lowest breakdown voltage of 841 V. The results show that the aspect ratio and the density of nanorods are the main factors influencing the breakdown behavior. Samples having lower breakdown voltage possess higher aspect ratios and densities. However, the $V_{Al}/V_{Ti} = 10$ V/100 V specimen has a slightly higher breakdown voltage than the specimen with $V_{Al}/V_{Ti} = 20$ V/100 V although its density of nanorods is higher than the specimen with $V_{Al}/V_{Ti} = 20$ V/100 V. This may be attributed to the following reasons. For the AAO nanopores fabricated at 10 V in the first anodization process, the pore density was higher than those prepared by 20 V. However, the nanopores may not be isolated from one another as shown in Fig. 8. During the second anodization process, the TiO$_2$ nanorods may thus touch one another when they grew higher. The other possibility is that the nanorods in Fig. 8 have a high aspect ratio of 10.28 and the distance between the neighboring nanorods is very small. Therefore, nanorod arrays fabricated at $V_{Al}/V_{Ti} = 10$ V/100 V were not vertically stood on the substrate, resulting in a higher working voltage. The results under nitrogen, argon and oxygen atmospheres show the same trend as CO$_2$. Therefore, they are not shown here.  

We then chose the sample having the lowest breakdown voltage ($V_{Al}/V_{Ti} = 20$ V/100 V) to examine its breakdown properties under different atmospheres. Figure 9 shows the breakdown voltages of Ar, N$_2$, O$_2$, and CO$_2$ at a chamber pressure of 10$^3$ Pa at room temperature. Each gas obtains a different breakdown voltage. Argon atmosphere shows the lowest breakdown voltage (301 V) followed by nitrogen (419 V) and oxygen (516 V). Carbon dioxide shows the highest breakdown voltage (605 V). Each breakdown voltage corresponds to a specific gas, which means it has a great selectivity of sensing gases. From the results, the working voltage is about 600 V for a physical gas sensor using TiO$_2$ nanorod arrays fabricated by anodizing superimposed metallic layers method as the anode under electrode separation of 579 $\mu$m.  

From the results published by previous researchers, the breakdown voltage is a function of anode-cathode separation distance.

### Table II. The density and aspect ratio of the TiO$_2$ nanorods under different anodizing conditions.

<table>
<thead>
<tr>
<th>$V_{Al}$ / $V_{Ti}$</th>
<th>10 / 100</th>
<th>20 / 100</th>
<th>40 / 100</th>
<th>60 / 100</th>
<th>40 / 40</th>
<th>40 / 60</th>
<th>40 / 80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ($\times 10^{-9}$)</td>
<td>81.5 cm$^{-2}$</td>
<td>36.3 cm$^{-2}$</td>
<td>13.1 cm$^{-2}$</td>
<td>7.71 cm$^{-2}$</td>
<td>13.1 cm$^{-2}$</td>
<td>13.1 cm$^{-2}$</td>
<td>13.1 cm$^{-2}$</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>10.27</td>
<td>5.22</td>
<td>3.35</td>
<td>3.08</td>
<td>1.30</td>
<td>1.91</td>
<td>2.67</td>
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which means higher electrode separation results in larger breakdown voltage. In order to compare the gas sensor efficiency with others more precisely, we calculate the electric field defined by the working voltage divided by the distance between two electrodes. The working voltage is 600 V and the distance between two electrodes is 579 μm. The calculated electric field across the TiO2 nanorod arrays is about 1.03 V/μm. Compare to other gas sensor devices using different anode materials, such as CNT arrays (3 V/μm) and ZnO (5 V/μm) nanowires, the TiO2 nanorods demonstrated a higher efficiency compared with the other two materials. Therefore, we can fabricate TiO2 nanorod arrays and obtain desired aspect ratios and density by controlling the anodizing conditions. Furthermore, the fabricated TiO2 arrays have shown to possess a good selectivity and low working electric field for gas sensing.

Conclusions

In summary, we successfully fabricate TiO2 nanorod arrays by a two-stage anodization process using double-layered metals. The major advantage of the process is that it is direct, easy and low cost. By changing the anodizing conditions of aluminium (first stage of anodization process) and titanium layer (second stage of anodization process), the density and aspect ratio of TiO2 nanorods can be well controlled. XPS analysis suggested that nanorod arrays were composed of titanium dioxide and a small amount of aluminium oxide on the surface. TiO2 nanorod arrays were further explored as the field ionization anode. When the density and the aspect ratio of nanorods become larger, the efficiency of gas sensing improves. The sensor also shows good selectivity and low working electric field. Therefore, TiO2 nanorod arrays fabricated by anodization have a high potential for application in gas sensing.

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References