Fabrication of TiO$_2$ sensor using rapid breakdown anodization method to measure pressure, humidity and sense gases at room temperature

Reem Saadi Khaleel, Mustafa Shakir Hashim*
Department of Physics, Education College, Mustansiriya University, Baghdad, Iraq

Abstract
Rapid breakdown anodization (RBA) process was used to fabricate TiO$_2$ sensor to measure pressure and humidity and sense gases at room temperature. This chemical process transformed Ti to its oxide (TiO$_2$) as a powder with amorphous phase as X ray diffraction (XRD) technique confirmed. This oxide consisted from semi spherical nanoparticles and titania nanotubes (TNTs) as Scanning electron microscope (SEM) technique showed. TiO$_2$ powder was deposited on Ti substrates by using electrophoretic deposition (EPD) method. Average pressure sensitivity was 0.34 MΩ/bar and hysteresis area was 1.4 MΩ .bar. Resistance of TiO$_2$ decreased exponentially with the increasing of relative humidity (RH%). The sensitivity% of TiO$_2$ for RH% was greater than 70% in the range of (50-95). TiO$_2$ was tested as a sensor for Ammonia, Ethanol and Methanol. Its sensitivity and selectivity towards Ammonia were the greatest but the shortest response and recovery times were recorded toward Methanol.

Keywords: Rapid breakdown anodization, TiO$_2$, sensor, humidity, Ammonia and Ethanol.

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1- Introduction:
Nano structured metal oxide semiconductor sensors had better sensing response due to its small size and increased surface-to-volume ratio [1]. Mutable techniques were developed by scientists to synthesize different materials with nano dimensions like nanotubes, nanolayers and nanoparticles. The controlling of nanomaterials' properties is challenging within nanotechnology and nanoscience and fabrication of highly efficient nanostructures in easily controllable manner and a cheap tuneable is of high technological and scientific interest [2].

Rapid breakdown anodization (RBA) process is one of the methods that produce titania nanotube powder with relatively long tall up to several micrometers. In this normal anodic process, chemical solution contains usually fluoride based electrolytes, water and glycerin or ethylene glycol were used by applying voltage between two immersed electrodes in this solution [3]. But one of the limitations of TNTs by this technique is its sticking on titanium substrate. This drawback prevents using these nanotubes on other substrates. Efforts were focused to synthesize TNTs in powder form [4] in order to deposit it on desired bodies by different coating methods. Antony et al. explained in details the steps of creation TiO$_2$ nanotubes powder by using perchloric acid [5]. Obtaining TNTs in percloric acid solution by anodization process was reported by many groups [6-8]. These works tried to get titania with different dimensions by using variable conditions like changing the applied voltage or using chloride containing organic and inorganic acid solutions.

There were multiple works on utilizing the products of the normal anodization process as gas sensors, but at the best of our knowledge, there are no papers used the products of RBA as Ammona, Ethanol and Methanol sensors. David et al. used RBA to fabricate Hydrogen sensing of Pt loaded TiO$_2$ nanotubes powders. At room temperature their sensor showed a linear response to hydrogen concentration [9].

One of the most current crucial issues in the world is atmospheric pollution. So the development of good sensors to detect harmful and toxic gases becomes an active scientific field. The improvement of low cost and portable sensor gas with selectivity, low working temperature and high sensitivity is still a great challenge [10]. Semiconducting metal oxides are good candidates for gas sensing due to the changing of their electrical conductivity during the explosion to active gases [11]. Resistance type metal oxide gas sensors have multi advantages like excellent sensitivity to the great majority of gases, simple manufacturing approaches, and low cost [12].

In current work, an attempt was introduced to fabricate single pressure, humidity and gas sensor by using produced TiO$_2$ powders by RBA process.

2- Materials and methods
2-1 Preparation of TiO$_2$ powder
The procedure of TiO$_2$ powder synthesizing by RBA technique was mentioned by Park et al. [8] After cleaning with alcohol; Ti foil (0.1 mm thick), with rectangular shape (1x2 cm) was immersed in 0.1 M HClO$_4$ electrolyte. In anodization process two Ti pieces were used; one as a working electrode and the second as a counter. The distance between the two electrodes was 0.5 cm and applied voltage between them was 20 volts. The time of anodic process was one hour. In this period Ti piece was transformed completely to white powder. The wet powder was dried by a hot plate.

2-2 Deposition of producing powders
Produced powder (1gm) was added on artificial ethanol (5ml) then the mixture was stirred for 30 minutes. By using EPD technique the suspended particles were deposited on the surface of Ti plate after applying 100 volts between the two electrodes for one minute. The deposited layer was dried by putting them on a hot plate for 30 minutes. TiO$_2$ was annealed at 600°C for two hours.

2-3 Surface and structure characterization of producing layer
The produced layer was tested by XRD techniques and the topography of its surface was pictured by atomic force microscopy (AFM) technique. SEM images were used to evaluate the particle sizes and their appearances.

2-4 Humidity and pressure measurements
1 liter class container was utilized to test the response of a TiO$_2$ sample to humidity and pressure. Controlling of humidity inside the container was done by using two salts; K$_2$SO$_4$ to increase relative humidity (%RH) from 10% to 100% and KOH to reduce it down to 10%. Hygrometer (type KT-908) was used to measure %RH. Air pressure inside the container was increased by a simple air
motor and the decreasing was done by using the valves that control the input and output of gases in the container. Gas pressure was measured inside the container by using pressure gauge type (WIKAI).

2-5 Gas sensor system

This system consists of: sealed chamber made from stainless steel with capacity 6 liters, controlled vacuum system to evacuate the chamber from gases after test and an ohmmeter to measure sample’s resistance. To enter gas inside the chamber appropriate chemical solution was evaporated inside the external unit and then transfer produced gas to the chamber. To evaporate a small chemical solution and produce an appropriate gas amount micropipette type (DRAGONMED) was used. Ammonia was produced by evaporating NH₃OH solution (Scharlau-Spain, 32% concentration) according to the following equation [1]:

\[ \text{NH}_3\text{OH (aq)} \rightarrow \text{NH}_3\text{(gas)} + \text{H}_2\text{O(l)} \]

Also Ethanol and Methanol liquids were used to produce their vapors.

3- Results and discussion

3-1 Materials characterization

Figure-1 shows XRD patterns of as prepared TiO₂ powder before and after the annealing process at 600°C for 2 hours. Produced TiO₂ powder by RBA had an amorphous structure but after heat treatment, it transformed to crystalline TiO₂ with Anatase phase (PDF Card no. 00-021-1272). There was a trace of Ti element that not transformed into its oxide. Ti (101) peak confirmed the existence of this element after the annealing process.

![Figure 1-XRD pattern of TiO₂ powder before and after annealing](image)

Figure-2 shows AFM images and granularity cumulating distribution chart on the surface of as deposited TiO₂.

![Figure 2-The topographies and granularity cumulating distribution of TiO₂, A: 3D view, B: 2D view and C: percentage(%) versus diameter (nm).](image)
Roughness average and grain size were 4.43 nm and 87.82 nm respectively. Figure-3 shows different SEM images of as deposited TiO\(_2\). Image A and D show the formation of TNTs bundles with length equals to about 1μm. Image B and C show that the nanoparticles constitute the nanotubes' walls. This result is in agreement with that reported by Antony et al. [5].

![Figure 3-SEM images of as deposited TiO\(_2\).](image)

AFM and SEM images show that morphology had both nanoparticles and nanotubes. The appearance of bundles made of tightly packed tubes (as shown in image D Figure-3) is observed also by Panaitescu et al [2].

3-2 Sensing characterization

3-2-1 Pressure sensing

Figure-4 shows the variation of resistance as a function of pressure's increasing and decreasing for TNTs powder. Increasing curve in Figure-4 consists of two regions the first region is linear (at low pressure values) and the second one is saturation region (at high pressure values). So the performance of this sensor is better at low pressures. Calculated average sensitivity is 0.34 MΩ/bar and hysteresis area is 1.4 MΩ.bar.
3-2-2 Humidity sensing

For humidity sensing applications TiO₂ is a promising material in thin and thick film forms. Compared with other phases the anatase phase has the high response to adsorbents [13]. Also because of their hydrophilic properties TiO₂ humidity sensors have been broadly studied [14]. Figure -5 illustrates the variations of resistance as a function to humidity for the TiO₂ oxide.

\[ R_{50} = \frac{100}{x} \]

This result coincides with that obtained by Gapale et al.[15]. This group found that the resistance of TiO₂ decreased exponentially with the increasing of RH%. At lower RH% the resistance decreased quicker than at higher RH%.

The sensitivity of the TiO₂ sensor for humidity can be defined as follows [16].

\[ S = \frac{R_{Humid} - R_{Dry}}{R_{Dry}} \times 100 \]

where \( R_{Humid} \) and \( R_{Dry} \) are the resistance at 95% to 10% RH and resistance at 10% RH, respectively. Figure-6 shows the sensitivity of TiO₂ at different humidity levels.
Figure 6-the sensitivity (%) of TiO$_2$ sensor for different relative humidity.

Lower sensitivity of the TiO$_2$ sensor at low RH% values can be attributed to the filling of larger sized pores with water vapor and then the condensation of them on its walls resulting in the filling of all empty areas of the pores [15].

3-2-3 Gas sensing

Figure-7 shows the variation of $R_{gas}/R_{air}$ with time as a function to different concentrations of Ammonia, where $R_{gas}$ and $R_{air}$ are the resistance of TiO$_2$ in the gas and air atmosphere respectively. After injection of Ammonia gas, this ratio decreased and after stability, it increased when the gas was withdrawn outside the testing chamber. This result in agreement with that obtained by Liu et al.[16]. After the injection of NH$_3$ gas the observed decrease of TiO$_2$ resistance is due to the electron donation from NH$_3$ to TiO$_2$. In air atmosphere, as deposited TiO$_2$ absorbs the O$_2$ molecules on its surface, producing chemisorbed oxygen species such as $O_2^-$. At room temperature and when exposed to reducing Ammonia gas its molecules are firstly adsorbed on the surface of the TiO$_2$. Then these molecules react with the $O_2^-$ ions. After the redox reaction, many numbers of electrons return back to TiO$_2$ surface and finally its resistance became smaller. The surface reactions between adsorbed $O_2^-$ ions and NH$_3$ gas can be described as follows [17].

$$2NH_3 + 3O_2^- (ads) \rightarrow 3H_2O + 3e^- + N_2$$

Figure 7-the variation of $R_{gas}/R_{air}$ with time due to interaction with Ammonia gas.

There are two significant indexes of any gas sensor: response time and the recovery time. The first one is the time to reach 90% of the maximum sensing response with respect to the target gas injection. The second one is the time to recovery to 10% of the maximum sensing response with respect to the target gas removal [18]. Table-(1,2) shows the variation of response and recovery times with different Ammonia concentrations. Both time increased with the increasing of ppm values.
Table 1-Response and recovery times as a function to Ammonia concentrations

| Ammonia concentration (ppm) | Response time (sec) | Recovery time (sec) |
|----------------------------|---------------------|---------------------|
| 5                          | 17.7                | 40.2                |
| 10                         | 18.2                | 45                  |
| 20                         | 31.5                | 48.3                |

Figure-8 shows the variation of $R_{\text{gas}}/R_{\text{air}}$ with time as a function to different concentrations of Methanol. The variations of this ratio look like that with Ammonia.

![Figure 8-R_{\text{gas}}/R_{\text{air}} vs. time due to interaction with Methanol](image)

Both response and recovery times increase with increasing of Methanol concentration.

Table 2-Response and recovery times as a function to Methanol concentrations

| Methanol concentration (ppm) | Response time(sec) | Recovery time(sec) |
|-----------------------------|--------------------|--------------------|
| 5                           | 13.3               | 8                  |
| 10                          | 17.8               | 11.3               |
| 20                          | 18                 | 18.4               |

Figure-9 shows the variation of $R_{\text{gas}}/R_{\text{air}}$ with time as a function to different concentrations of Ethanol. Vanaraja et al. proved that on the TiO$_2$ surface ethanol molecules interact more speedily with adsorbed oxygen species than the other molecules. At room temperature the likely chemical reaction for ethanol is as follows [19]:

$$O_2 + e^- \leftrightarrow O_2^{\text{ads}}$$
$$C_2H_5OH + 3O_2^{\text{ads}} \leftrightarrow 2CO_2 + 3H_2O + 3e^-$$

After inserting the ethanol, it interacts with adsorbed $O_2^{\text{ads}}$ and frees the trapped electrons back to the TiO$_2$ surface resulting in decreasing in resistance [20]. Figure-9 illustrates that with the increase in injected ethanol concentrations, $R_{\text{gas}}$ varies greatly from its base resistance ($R_{\text{air}}$). This might attribute to the catalytic effect of TiO$_2$ nano particles (see Figure-3), which consolidate the interaction between ethanol and oxygen species by increasing the number of the adsorbed oxygen at room temperature [21].
Both response and recovery times decrease with increasing of Ethanol, see Table-3. This behavior is in contrast with that for Ammonia and Methanol.

| Ethanol concentration (ppm) | Response time (sec) | Recovery time (sec) |
|-----------------------------|---------------------|---------------------|
| 5                           | 27                  | 3.5                 |
| 10                          | 18                  | 18.6                |
| 20                          | 15.2                | 24.8                |

Figure-10 shows the sensitivities of TiO₂ sensor to Ammonia, Methanol and Ethanol gases. The sensitivity(%) to Ammonia is the largest one.

Figure-11 shows calculated selectivity towards Ammonia, Ethanol and Methanol. The values of selectivity were calculated by using the following equation[ 22].

\[
Sel_{gas1}(\%) = \frac{S_{gas1}}{S_{gas1} + S_{gas2} + S_{gas2}}
\]
Where $S_{\text{gas1}}$, $S_{\text{gas2}}$ and $S_{\text{gas3}}$ are the responses exhibited by the TiO$_2$ sensor towards testing gases at room temperature.

Figure 11-calculated selectivity of TiO$_2$ towards test gases.

Figure-11 shows that TiO$_2$ sensor was highly selective to Ammonia compared with that for Ethanol and Methanol.

Conclusions
Because the coexistence of nanoparticles and nanotubes are as a product of RBA; this technique is an active method to fabricate humidity and pressure sensors and sense different gases with acceptable sensitivities.

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