Fabrication of TiO₂ sensor using rapid breakdown anodization method to measure pressure, humidity and sense gases at room temperature

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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.

تصنيع متحسس TiO_2 لقياس الضغط والرطوبة وتحسس الغازات بدرجة حرارة الغرفة بأستخدام طريقة أنودة الانهيار السريع

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الخلاصة

    أستخدمت عملية أنودة الانهيار السريع لتصنيع متحسس TiO_2 لقياس الضغط والرطوبة وتحسس الغازات بدرجة حرارة الغرفة. حولت هذه العملية الكيميائية التيتانيوم الى أوكسيد التيتانيوم كمسحوق بطور عشوائي كما أثبتت فحوصات الاشعه السينية. تألف هذا الاوكسايد من جسيمات نانوية شبه كروية و أسطوانات نانوية. رسب مسحوق أوكسيد التيتانيوم على قواعد من التيتانيوم باستخدام الترسيب بطريقة الهجرة الكهربائية. كان معدل حساسية الضغط 0.34 MΩ/bar وكانت مساحة الهسترة 1.4 MΩ. bar . تناقصت مقاومة ال TiO_2 أسياً مع زيادة الرطوبة النسبية. كانت حساسية ال TiO_2 للرطوبة النسبية أكبرمن 70% بالمدى (50−95). أختبر ال TiO_2 كمتحسس للأمونيا , الأيثانول و الميثانول. كانت حساسية وأنتقائية ال TiO_2 للامونيا هي الاكبرولكن كانت أوقات الأستجابة والاستعادة هي الاقصر للميثانول.

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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 perchloric 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 600^0C 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_2SO_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 NH_4OH solution (Scharlau-Spain, 32% concentration) according to the following equation [1]:

NH_4OH (aq) $\rightarrow NH_3$(gas) + H_2O(l)
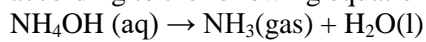
Also Ethanol and Methanol liquids were used to produce their vapors.

3- Results and discussion

3-1 Materials characterization

   Figure-1 shows XRD patterns of as prepared TiO_2 powder before and after the annealing process at 600^0C for 2 hours. Produced TiO_2 powder by RBA had an amorphous structure but after heat treatment, it transformed to crystalline TiO_2 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.
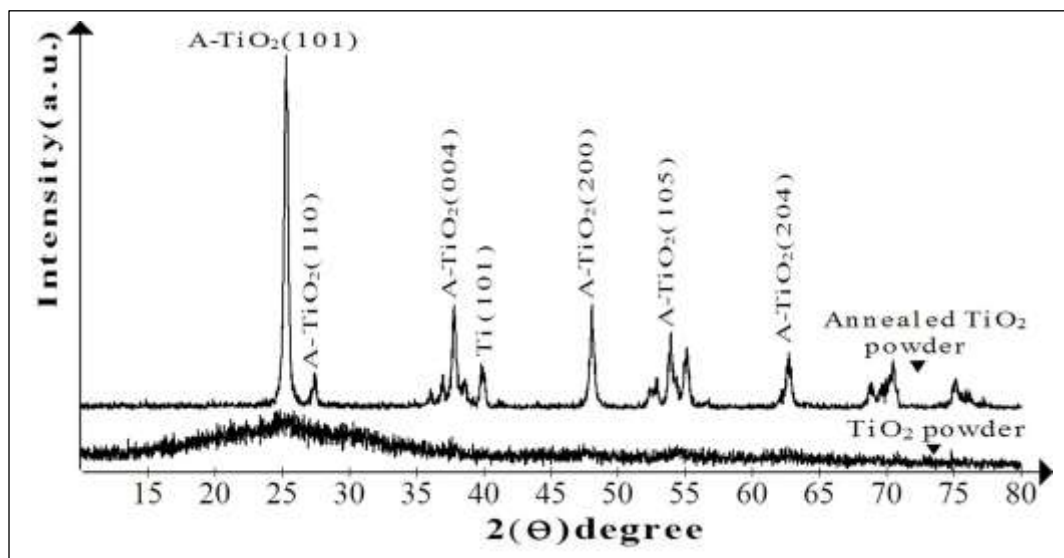

Figure 1-XRD pattern of TiO_2 powder before and after annealing

 Figure-2 shows AFM images and granularity cumulating distribution chart on the surface of as deposited TiO_2 .
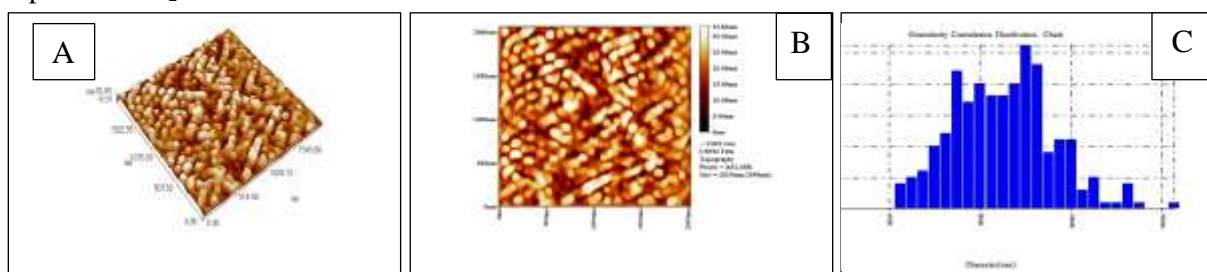

Figure 2-The topographies and granularity cumulating distribution of TiO_2, A: 3D view, B: 2D view and C: percentage(%) versus diameter (nm).

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].
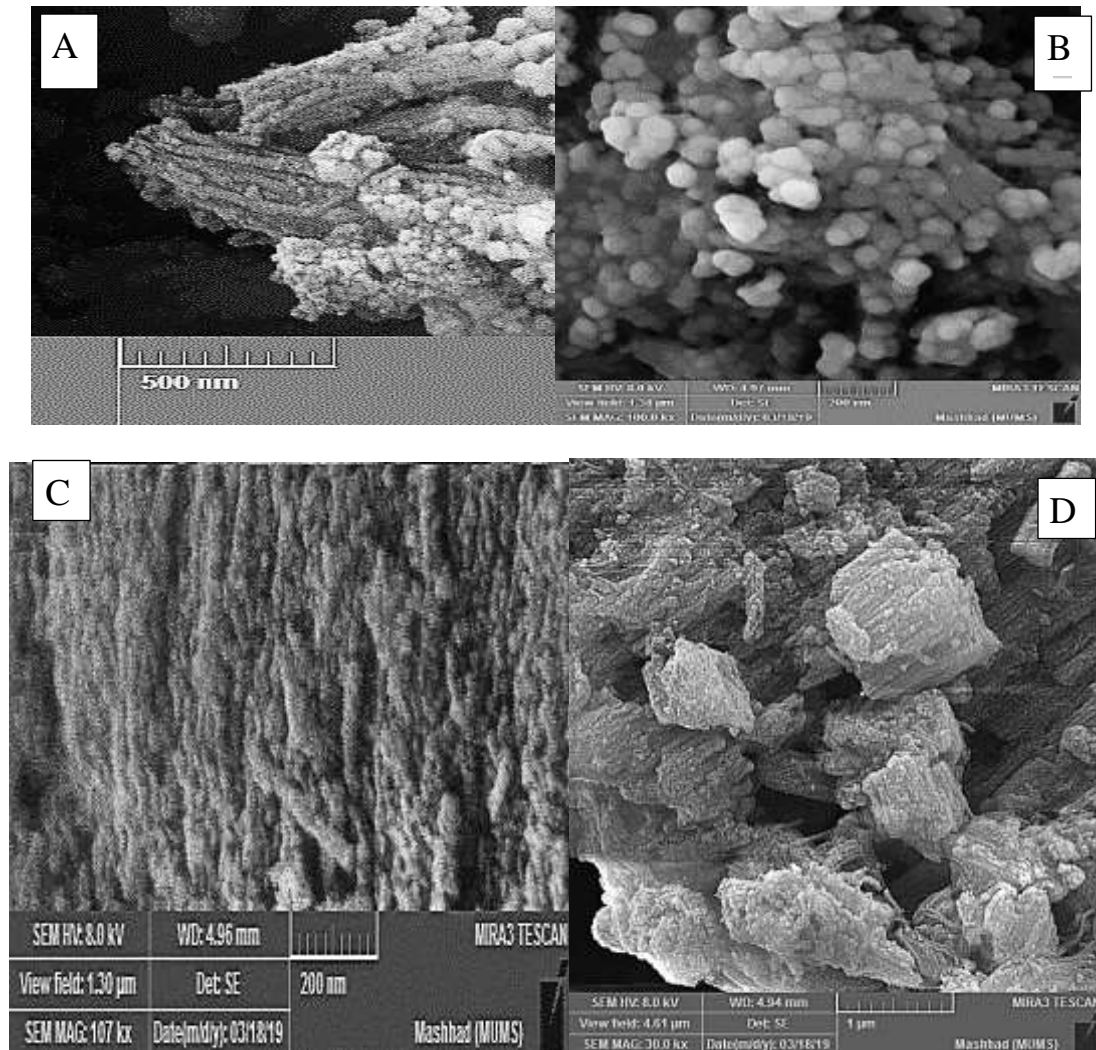

Figure 3-SEM *images of as deposited TiO₂.*

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.
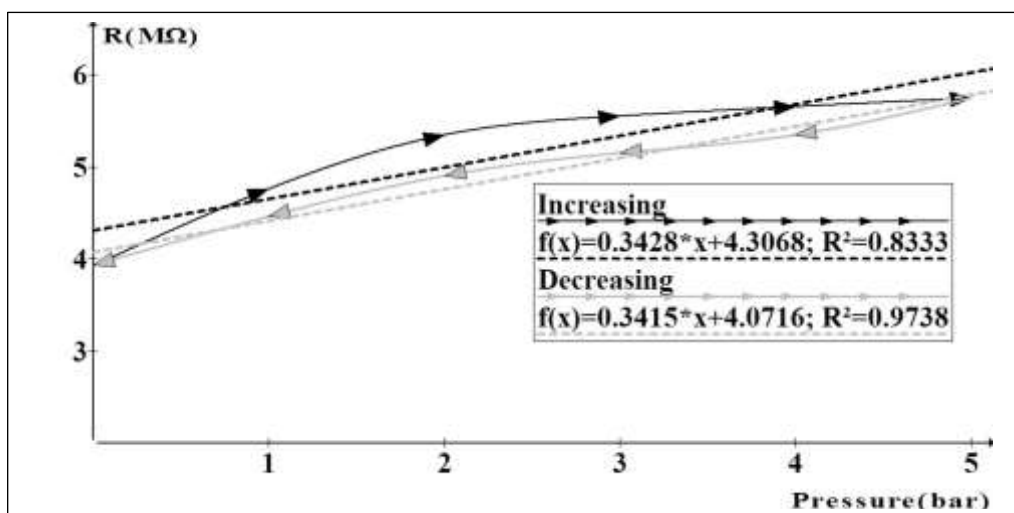
Figure 4-the variation of resistance as a function of pressures with fitting

3-2-2 Humidity sensing

For humidity sensing applications TiO_2 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 TiO_2 humidity sensors have been broadly studied [14]. Figure -5 illustrates the variations of resistance as a function to humidity for the TiO_2 oxide.
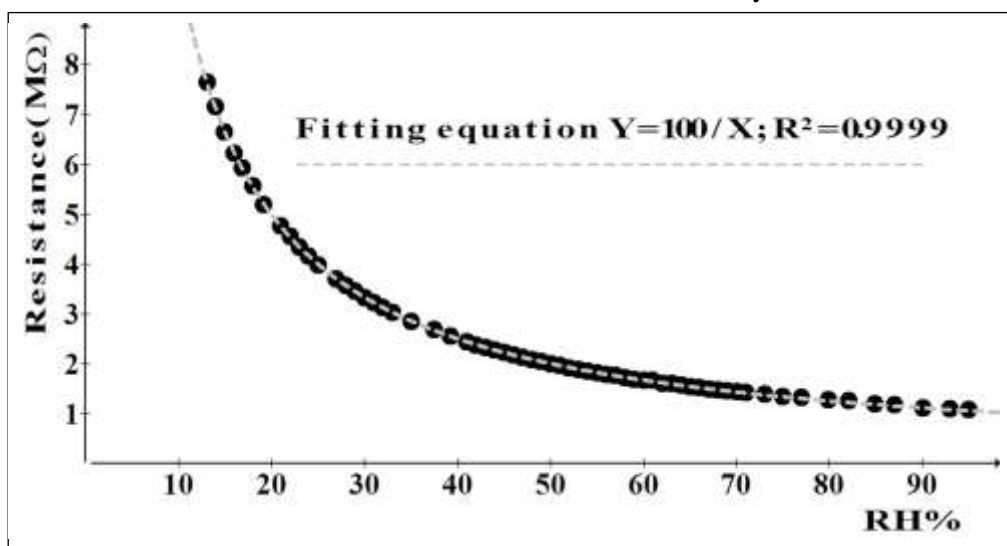

Figure 5-The resistance variation with RH% of TiO_2 with fitting

RH% varies inversely with humidity and fits exactly with the equation Y=100 / X. This result coincides with that obtained by Gapale et al.[15]. This group found that the resistance of TiO_2 decreased exponentially with the increasing of RH%. At lower RH% the resistance decreased quicker than at higher RH%.

The sensitivity of the TiO_2 sensor for humidity can be defined as follows [16].

$$S = \frac{R_{Humid} - R_{Dry}}{R_{Dry}} * 100$$

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 TiO_2 at different humidity levels.
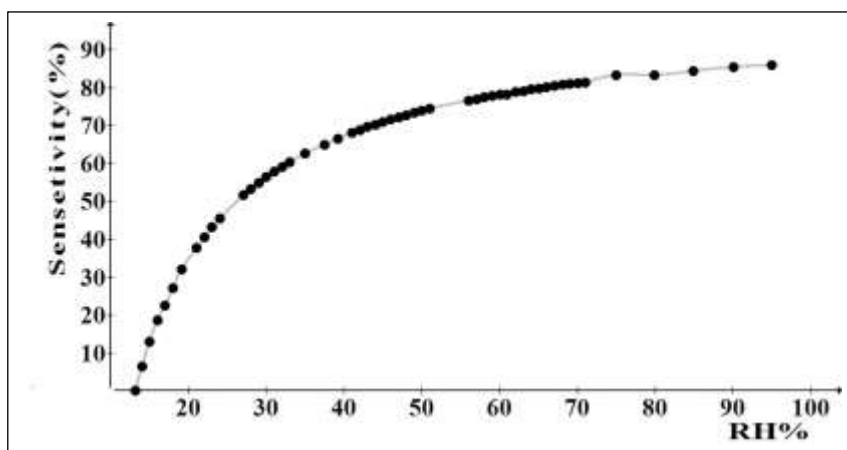
Figure 6-the sensitivity (%) of TiO$_2$ sensor for different relative humidity.

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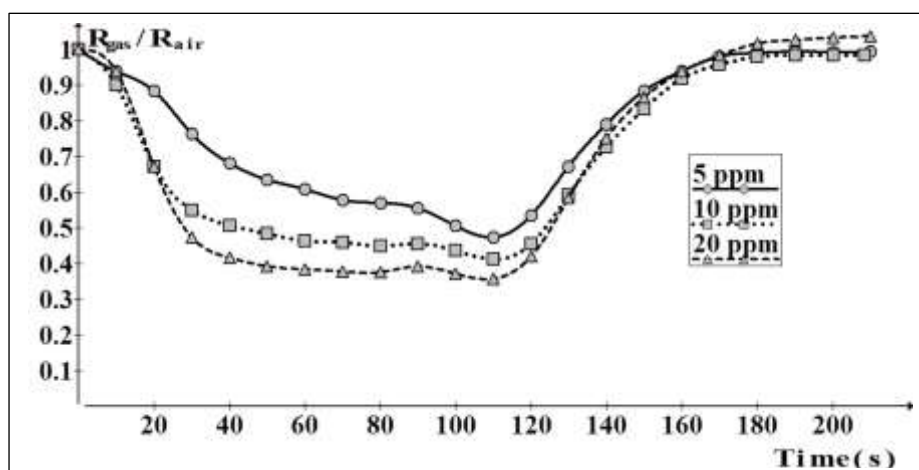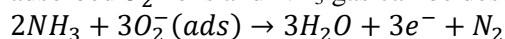
$$2NH_3 + 3O_2^-(ads) \rightarrow 3H_2O + 3e^- + N_2$$

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] .Tables-(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_{gas}/R_{air} with time as a function to different concentrations of Methanol. The variations of this ratio look like that with Ammonia.
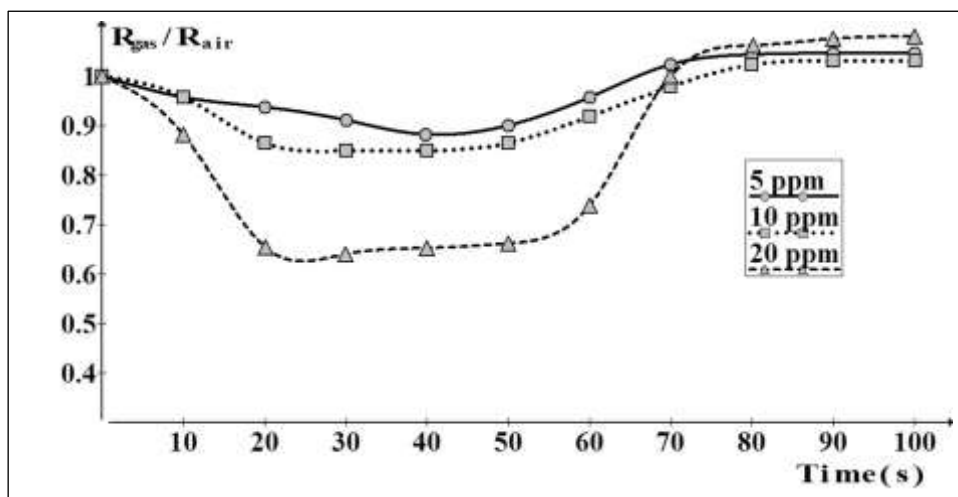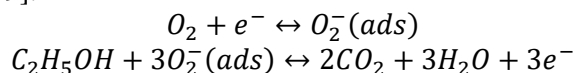

Figure 8-R_{gas}/R_{air} vs. time due to interaction with Methanol

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_{gas}/R_{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]:

$$O_2 + e^- \leftrightarrow O_2^-(ads)$$
$$C_2H_5OH + 3O_2^-(ads) \leftrightarrow 2CO_2 + 3H_2O + 3e^-$$

After inserting the ethanol, it interacts with adsorbed O_2^- 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_{gas} varies greatly from its base resistance (R_{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].
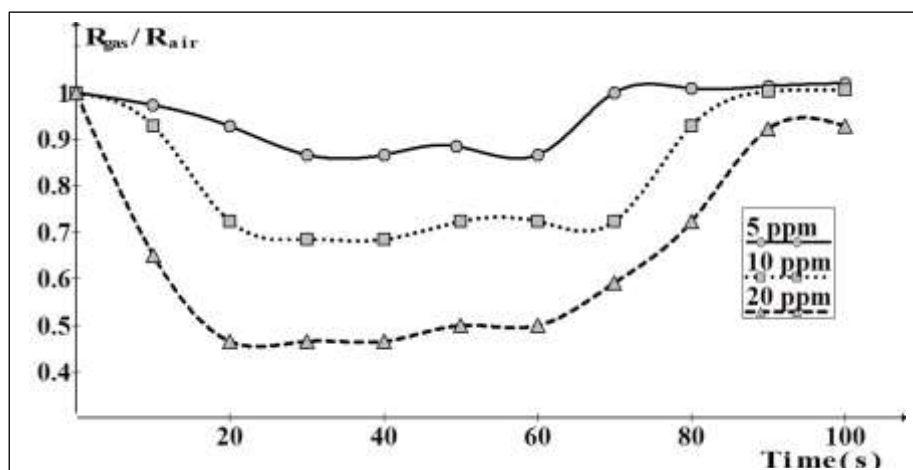
Figure 9-R_{gas}/R_{air} vs. time due to interaction with Ethanol

Both response and recovery times decrease with increasing of Ethanol, see Table-3. This behavior is in contrast with that for Ammonia and Methanol.

Table 3-Response and recovery times as a function to Ethanol concentrations

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 TiO_2 sensor to Ammonia, Methanol and Ethanol gases. The sensitivity(%) to Ammonia is the largest one.
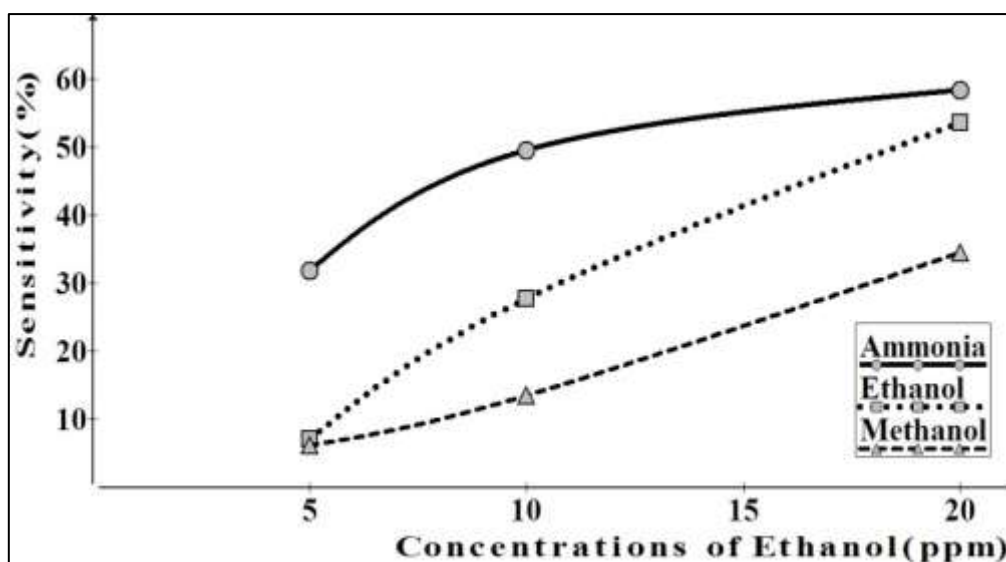

Figure 10-the sensitivities of TiO_2 sensor to three test gases.

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_{gas1}, S_{gas2} and S_{gas3} are the responses exhibited by the TiO_2 sensor towards testing gases at room temperature.
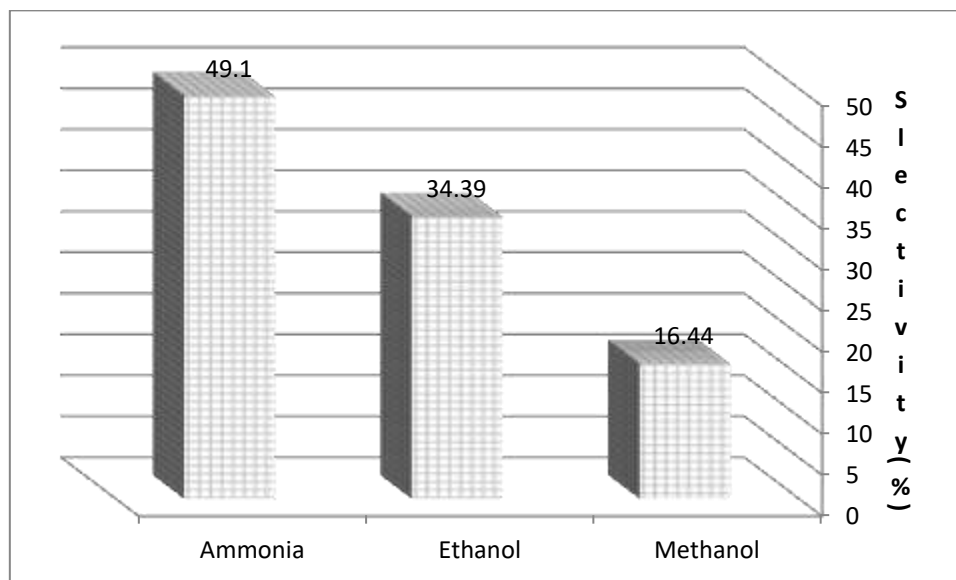

Figure 11-calculated selectivity of TiO_2 towards test gases.

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.

References
1. Lyson-sypien B., Czapla A., Lubecka M**. 2012.** Nanopowders of chromium 172 doped TiO_2 for gas sensors. *Sensors Actuators B Chem*. **175**: 163-172.
2. Panaitescu E. , Richter C. and Menon L. **2008 .** A study of titania nanotube synthesis in chloride-ion-containing media. *Journal of The Electrochemical Society*, **155**(1): E7-E13.
3. Hashim M., Alzubaydi Th. Mali S. **2013.** Corrosion characterisation of medical alloys modified by forming titanium nanotubes via anodic oxidation and annealing process. *Materials Technology*, **28**(6): 297-304.
4. Allam N. , and Grimes C. **2007.** Formation of Vertically Oriented TiO_2 Nanotube Arrays using a Fluoride Free HCl Aqueous Electrolyte, *J. Phys. Chem. C* . **111**: 13028-13032.
5. Antony R., Mathews T., Dasgupta A., Dash S., Tyagi A.K. and   Raj B. **2011.** Rapid breakdown anodization technique for the synthesis of high aspect ratio and high surface area anatase TiO_2 nanotube powders. *Journal of Solid State Chemistry,* **184**: 624–632.
6. Nakayama K.,   Kubo T., Asano T., Tsubokura A., and Nishikitani Y. **2005.** 20[8th] The Electrochemical Society Meeting Abstracts. Vol. 2005-2, Los Angeles.
7. Ali S., Orell O., Kanerva M. and Hannula S. **2018.** Effect of Morphology and Crystal Structure on the Thermal Conductivity of TNTs. *Nanoscale Research* Letters.**13**: 212.
8. Park S., Paek Y., Lee H. and Kim Y. **2010.** Lithium Ion Insertion in Titania Nanotube Powders Synthesized by Rapid Breakdown Anodization, *Electrochemical and Solid-State Letters*, **13**(7): A85-A87.
9. David T., Sagayaraj P., WilsonP.,   Murugesan C. , Prabhu E. , Murthy A. and Annapoorani S. **2016.** Room Temperature Hydrogen Sensing of Pt Loaded TiO_2 Nanotubes Powders Prepared via Rapid Breakdown Anodization, *Journal of The Electrochemical Society*, **163**(3): B15-B18.
10. Galstyan V., Comini E., Faglia G. and Sberveglieri G. **2013.** TiO_2 Nanotubes: Recent Advances in Synthesis and Gas Sensing Properties, *Sensors* . **13**: 14813-14838. doi:10.3390/s131114813.

11. Lu, H., Li, F., Liu, G., Chen, Z., Wang, D., Fang, H., Lu G., Jiang, Z. and Cheng, H. **2008.** Amorphous TiO_2 nanotube arrays for low-temperature oxygen sensors, *Nanotechnology*. **19**: 405504 (7pp).

12. Lee, J.S., Kwon, O.S., Park, S.J., Park, E.Y., You, S.A., Yoon, Jang. H. **2011**. J. Fabrication of ultrafine metal-oxide-decorated carbon nanofibers for DMMP sensor application. *ACS Nano* . **5**: 7992–8001.

13. Zakrzewska, K. and Radecka, M. **2017.**TiO_2 -based nanomaterials for gas sensing influence of anatase and rutile contributions. *Nanoscale Res Lett*.**12**: 89.

14. Liang, J G., Kim, E S., Wang, C. **2018.** Thickness effects of aerosol deposited hygroscopic films on ultra sensitive humidity sensors. *Sens Actuators B*. **265**(15): 632.

15. Gapale D., Arote S., Palve B. and Borse R. **2018.** Influence of precursor solution concentration on the structural, optical and humidity sensing properties of spray-deposited TiO_2 thin films, *Journal of Semiconductors*. **39**(12): 122003.

16. Liu H., Shen W., Chen X. and Corriou J. **2018.** A high-performance NH_3 gas sensor based on TiO_2 quantum dot clusters with ppb level detection limit at room temperature. *Journal of Materials Science: Materials in Electronics*, doi.org/10.1007/s10854-018-9952-9.

17. Cannilla, C., Bonura, G., Frusteri, F., Spadaro, D., Trocino, S., Neri, G**. 2014.** Development of an ammonia sensor based on silver nanoparticles in a poly-methacrylic acid matrix. *J. Mater. Chem. C*. **2**: 5778.

18. Karunagaran, B., Uthirakumar, P., Chung, S.J., Velumani, S. and Suh, E.-K. **2007.** TiO_2 thin film gas sensor for monitoring ammonia. *Materials Characterization*. **58**: 680 – 684.

19. Shankar, P., Rayappan JBB. **2013.** Spray deposited nanostructured zinc oxide thin film as room temperature ethanol sensor - role of annealing. *Sens Lett*.11:1956-1959.

20. Wang, Z. and Liu, L. **2009.** Synthesis and ethanol sensing properties of Fe-doped SnO_2 nano fibers. *Mater Lett*. **63**: 917-919.

21. Wisitsoraat, A., Tuantranont, A., Comini E. **2009.** Characterization of n-type and p-type semiconductor gas sensors based on NiOx doped TiO_2 thin films. *Thin Solid Films*. **517**: 2775-2780.

22. Karthika, M., Manoj, V., Boomadevi S. **2015.** Highly selective acetaldehyde sensor using sol-gel dip coated nano crystalline TiO_2 thin film. *J Mater Sci Mater Electron*. DOI: 10.1007/ s10854-015-3041-0.