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Plasma Etching Techniques, For Enhancing The Titanium Dioxide Sensitivity To Ammonia Gas

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***Abstract*—This work tested the effect of a new suggested techniques to improve the sensitivity of TiO_2 film for ammonia gas which prepared by radio frequency (R F) magnetron sputtering. The structure and surface morphology of the film were investigated by x-ray diffraction (XRD), Scanning electron microscope (SEM) and Atomic force microscope (AFM). The results revealed that in room temperature the sensitivity of the treated film increased to 15% comparing with 3.5% for that untreated film at a concentration of gas 100 ppm. The enhancement of gas sensing furthermore high response time was indicated that the TiO_2 film suitable for the donor gases detection.**

***Keywords*—TiO_2 thin films, catalytic layer, R.F. magnetron sputtering system, gas sensors, ammonia gas, sensitivity.**

1. Introduction: Air pollution in toxic and dangerous gases has become the most important subject by many researchers. The scientists worked on developing sensors made of semiconducting materials for the detection of these gases. Semiconductors sensors such as TiO_2 widely used for detecting of toxic and dangerous gases. Most of the toxic and dangerous gases such as (CO, H_2, CH_4 and NH_3) called donor gases, because its donate electron to the surface of detector which increase the conductivity of it. Semiconductor detectors work in principle, when sorption of detected gas on the surface leads to change (mostly to decrease) the electric resistance of gas detector surface area [1-3]. For a high response Catalytic layer must absorb detected gas into sufficient and/or different depth that causes results, sorption-desorption process efficiency increase and hence responce efficiency increase of sensor as a whole [4-7].Many techniques have used to obtain TiO_2 thin films including, electrodynamics atomization [8], sol gel dip coating [9], pulsed laser deposition [10], ion beam sputtering [11], ion beam assisted electron beam evaporation [12], plasma assisted chemical vapor deposition [13] and RF magnetron sputtering [14]. In the present study the improvement of TiO_2 donor gas sensor have been investigated using a new suggested technique depending on etching of TiO_2 film surface by plasma.

2. Methodology: Titanium dioxide thick film was deposited on an alumina substrate by radio frequency magnetron sputtering method in vacuum 10-4 torr with thickness of 1000 nm and resistance in the range of 100 ohm per mm_2.

Structure of the film was investigated by an X-ray diffractometer (model SHIMADZU-6000) Cu Kα line (λ=1.5406A) with 2θ varying in the range of 20–60. The view of surface and morphology is analyzed using a scanning

electron microscope (SEM) JEOL model JSM 7400F and atomic force microscope (AFM) model (SPM Ntegra NT – MDT) .

The plasma etching process was used to remove the unnecessary layers from the film surface (remove small grains from surface). The plasma used vapour hexafluoride SF6 gas. The average processing time 20 minutes with etching rate 0.05μm/min at temperature surfaces (273 – 550) K. After the etching process, the value of the electrical resistance of TiO_2 films became in the range of (1.0 MΩ) due to the decreasing of thickness. The layer structure has approximately one size of grains with thicknesses of about (300 – 400) nm. The films resistance was measured by a Keithley 2400 electrometer. The response was defined as the ratio of the electrical resistance in air (Ra) to that in tested gas (Rg) with operation work temperature of 473K.

3. Results and discussion: Fig. 1 shows The XRD patterns of the TiO2 samples which prepared at room temperatures and after annealing at 773 K. the XRD patterns for samples prepared at room temperatures show only three peaks at 25.30 TiO2 (101) , 37.90 (004) and 480 anatase with grain size in range of (200-300) nm. These results are in good agreement with (ASTM) standard the standard TiO_2 [X-ray diffraction data file [N 1997 JCPDS prevalent]. The average crystallite size is obtained by Scherer relation:

$$D = k\lambda / (\beta Cos\theta) \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where D is the average crystallite size, k is the shape factor (its value here is 0.9, λ is the wavelength of the incident X-ray photons, θ is the Bragg's angle in degrees, and β is the full-width-at-half maximum of the preferred peak in radian[15-18] .

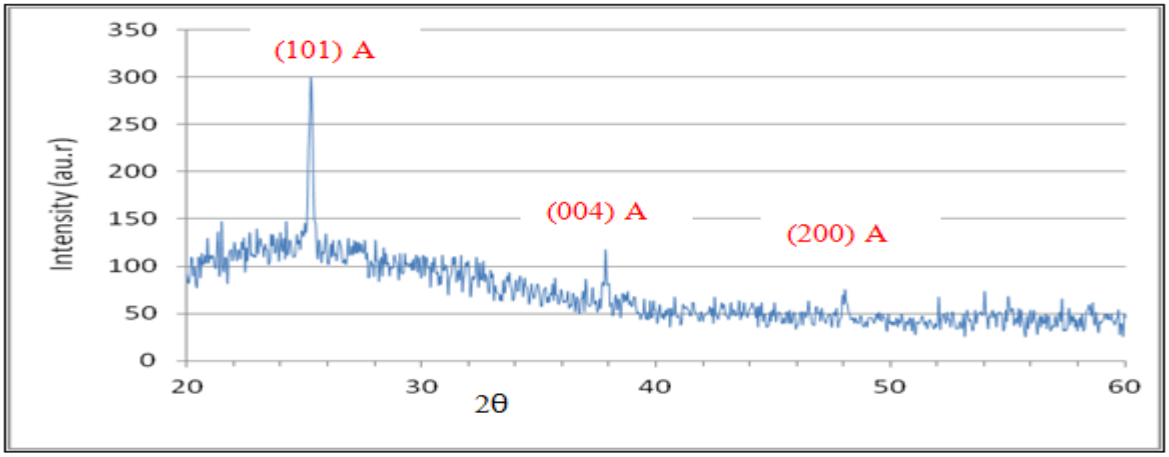
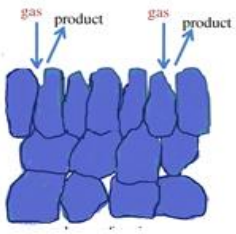


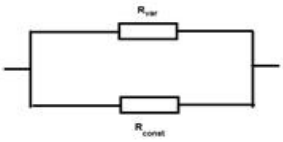
Fig.(1): XRD patterns of TiO_2 thin film prepared at R.T and annealed at 773 K

The mechanism and principal of gas layer resistance change are explained in the following: Internal areas of grain are strongly restored, so they have low electrical resistance. On the contrary, the resistance of a grain surface is very high. The grains contact with each other by surfaces. An electrical current proceeds in a film inside the grains as well as from grain to another.

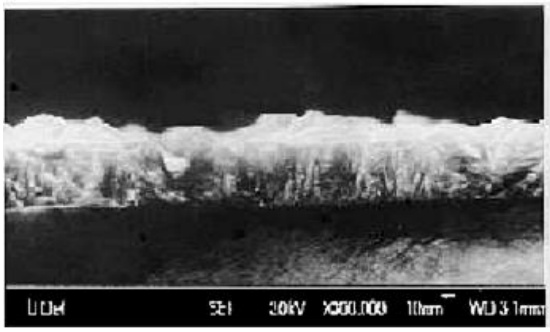
Thus it meets the superficial layer from stoichiometric of an oxide with high resistance. it follows, that the current periodically meets on the way sites with small resistance (internal areas of a grain) also cites with incommensurable by large resistance between grains(on grain surface. The final summation for two connected resistances: small and large. The small resistance is the sum of resistance of internal areas of grains, while the larger is the sum of resistance between the grains of intervals (R_{var}). The absorption of the detected gas through the film grains will not effect to change the internal resistance of the grains (R_{const}), but will affect to change the resistance between the grains (R_{var}).The Figure (2) shows the AFM and SEM images which are given the topography and the cross-section, respectively, of TiO_2 thin films after deposition before apply the new suggested technology. On the substrate surface, thin film structure is formed characterized by definite grain size commensurable with overall catalytic layer thickness. The initial resistance of catalytic layer R_{const} is by-passed by variable additional resistance R_{var} of surface area and parallel wiring scheme connection is realized in this case (Fig.2). The installation will make the total of electrical resistors (R_{const} and R_{var}) as a parallel electrical circuit. In this case, it will be (variable additional resistance) R_{var} is very weak.



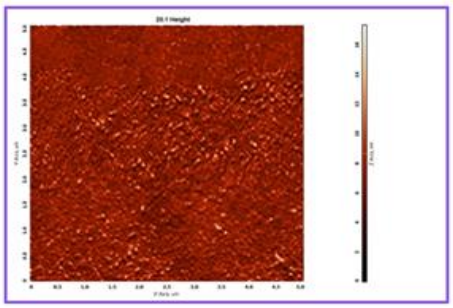
(a)Structure scheme of catalytic layer.



(b) Operation scheme of catalytic layer.



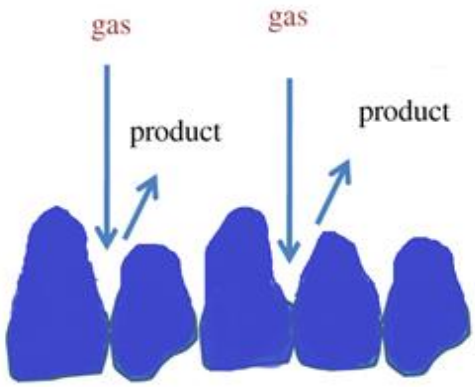
(c) SEM micrograph of TiO_2 catalytic layer on the substrate before treatment of surface.



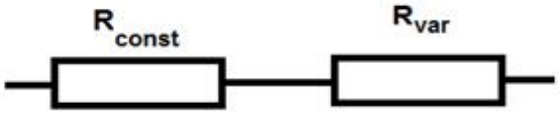
(d)AFM images on surface of TiO_2 catalytic layer before treatment.

Fig.2 Show the Common technology.

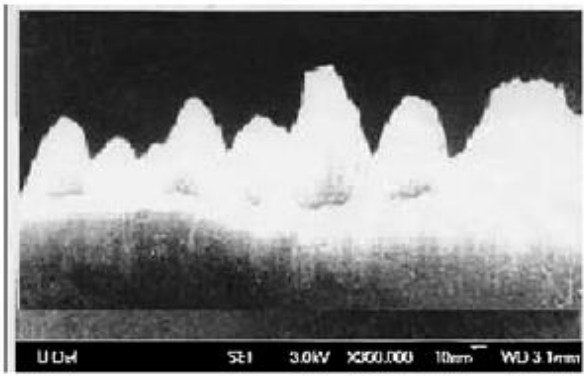
Scanning electron microscope image of TiO2 catalytic layer on the substrate and Atomic Force Microscope image of TiO2 catalytic layer after treatment by suggested technology (plasma etching) showed in figure (3) which illustrates the arrangement of grains of catalytic layer that it need to give more stability state to film structure by etching the small grains from the surface of film. The suggested technology allows obtaining sensors with the catalytic layer where the scheme of in a series circuit of resistors R_{const} and R_{var} is illustrating in Figure (3).



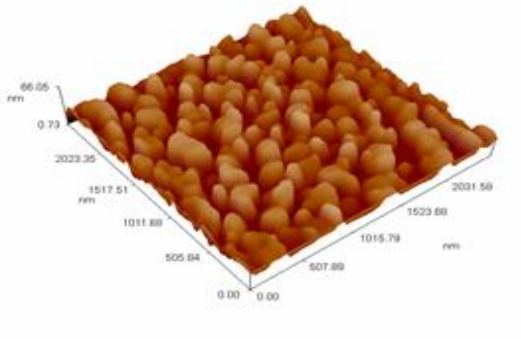
(a)Structure scheme of catalytic layer.



(b) Scheme of resistance modulation in catalytic layer along substrate surface.



(c) SEM micrograph of TiO_2 catalytic layer on the substrate after treatment of surface.



(d)AFM images on surface of treated TiO_2 catalytic layer.

Fig.3 the Suggested technology.

By the special technique of film deposition and the following treatment, we could realize the situation when inner grain areas (blue in Fig.3) have negligibly low resistivity Rconst compared to resistance R_{var} of the grain boundaries (light in Figure 3). It should be noted here that resistance of all catalytic layer is controlled by R_{var} value. It was clear the significant impact of the arrangement of the catalytic layer surface in this way in order to give a significant change in the surface resistance as a whole, which will increase the sensitivity of the sensor film. In accordance to suggested technology R_{var} can be obtained from any preliminarily determined value ("in situ" control) Figure (3).

Figure **(4)** shows the relation between the sensitivity of the thin film and operating time for TiO_2 films before surface treatment operation temperature (473 K) with different gas concentration. It was observed that the sensitivity of TiO_2 layers increased with increasing concentration of the gas.

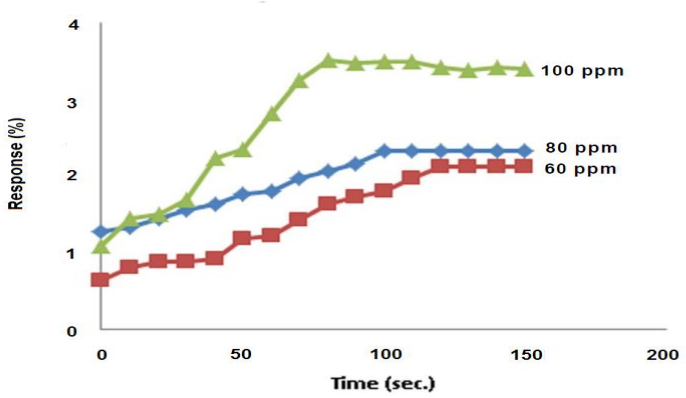


Fig. 4 Response curves of (TiO_2) thin films before surface treatment with different gas concentration at operation temperature (473 K).

After the treatment of TiO_2 films with the suggested technology, it can clearly observe that the response of catalytic layer became higher than before treatment of this film ,this behavior was noticed with all the concentrations of the used gas as in figure (5).

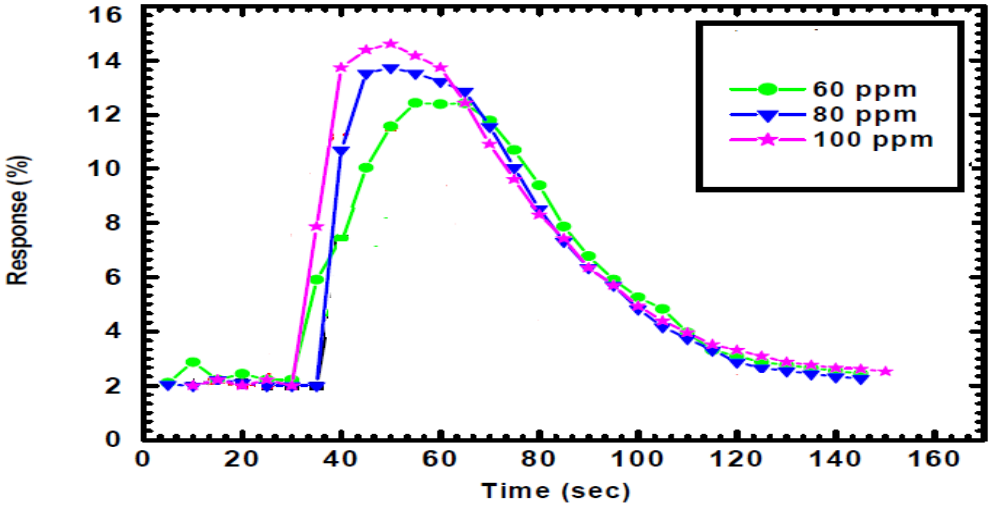


Fig. 5 Response curves of TiO_2 catalytic layer after surface treatment with suggested technology for different gas concentration at the optimum working temperature (473 K).

An attempt was made to study the sensitivity of TiO_2 films after treatment for the concentration of ammonia (60 – 100 ppm) as compared to the sensitivities for TiO_2 films before treatment. It was observed that TiO_2 catalytic layer with suggested technology can sense ammonia with a higher value of sensitivity as compared to untreated TiO_2 film in more than 3 times.

The sensitivity (S) of TiO_2 gas sensor was typically defined as the ratio of the surface resistance (Ra) of the film in air to that in the detected gas (Rg) [1-3]:

$$S = \left| \frac{Rg - R_a}{Ra} \right| \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The sensitivity of TiO_2 thin films for gas of concentration 100 ppm at operating temperatures (473 K) was shown in Figures (4 and 5). It was observed that the sensitivity for all samples increased with increasing the concentration of gas due to increasing of free charges carriers. From results obtained it was noticed that the resistance R_{var} after the etching process has become far greater than the value of the resistance R_{var} before treatment. After absorption of ammonia, the resistance will increase significantly, which will lead to a reduction in the value of the total resistance of the layer catalysts. The significant increase in the response and sensitivity of the layers of the film must be due to the arrangement of the resistances resistors (R_{const} and R_{var}). This new form of film surface (catalytic layer) gives great influence to change the overall resistance due to the change of resistance R_{var} when an ammonia vapor presences scheme of in a series circuit of resistors R_{const} and R_{var} is realized (Figures 3). The new structure of surface (catalytic layer) we could realize the situation when inner grain areas as in Figure 3, have negligibly low resistivity R_{const} compared to resistance R_{var} of the grain boundaries and it is meant in this case the resistance of all catalytic layers is controlled by R_{var} value. The low resistance at the presence of the gas will significantly affect the subtle resistance TiO_2 catalytic layer as a whole and increase connectivity providing this good response of TiO_2 catalytic layer.

4. Conclusion: For stability by removing the granules from the surface by plasma etching process of making the crystal microstructure of the surface to be a very effective to interact with the absorbed donor gases like ammonia. The gas sensitivity of the treated catalytic layers of ammonia vapour display massive increasing after treatment of TiO_2 films with a novel suggested technology. These results make the proposed technology applied in this research gave rise to enhance the performance of titanium dioxide films to be sensitive to the toxic and hazardous donor gases such as carbon oxide and ammonia or explosive gases such as methane.

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