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Hydrogen Sensor Based on Surface Activated WO3 Films by Pd Nanoclusters

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***Abstract*—**Tungsten trioxide has been prepared by using P-PTA as a precursor on alumina substrates by spin coating method. Palladium introduced on WO_3 film via electrolysis deposition by using palladium chloride as catalytic precursor. The catalytic precursor was introduced on the series of films with different morphologies. X-ray diffractometry (XRD), Scanning electron microscopy (SEM) and XPS were applied to analyze structure and morphology of the fabricated thin films. Then we measured variation of samples' electrical conductivity of pure and Pd added films in air and diluted hydrogen. Addition of Pd resulted in a remarkable improvement of the hydrogen sensing properties of WO_3 by detection of Hydrogen below 1% at room temperature. Also variation of the electrical conductivity in the presence of diluted hydrogen revealed that response of samples depends rather strongly on the palladium configuration on the surface.

***Keywords*—**Electrolysis, Hydrogen sensing, Palladium, WO_3

I. Introduction

HYDROGEN is a colorless, odorless and tasteless gas. It is light and has a large diffusion coefficient of 0.61 cm^2/s in air. Unlike fuels such as gasoline or diesel, hydrogen burns cleanly without release of pollutants or greenhouse gases. As a result, more attention is needed to be paid to hydrogen as a clean fuel in household and transportations applications. It is a highly flammable fuel with a wide combustion range of 4–75%. Therefore, detection and leakage control of this gas is a challenging subject. Today development of a hydrogen sensor with negligible power consumption, high stability, sensitivity and fast response is highly desired. Reports of various technologies for hydrogen sensing include, FETs [1]-[26] optical fibers [26] thermoelectric [2]-[12]; schottky diods [5, 21, 22]; surface acoustic wave devices [3]-[6] and metal oxides [7]. Metal oxide sensors are under intensive development and have been studied for decades. Simple construction, low cost, small size and high sensitivity with fast response are amongst their desirable properties. In these sensors, the thin layer in contact with a target gas would show response by changing its resistance [17]. WO_3 is one of the most widely used materials due to its fast response with high sensitivity towards different gases. It has been shown that the addition of an appropriate amount of metal additives promotes chemical reactions by reducing the activation energy between the film surface and the target gas. Also, it increases the response and selectivity as well as decreasing the maximum temperature of sensor response. In the hydrogen sensing case, modifying metal oxides especially WO_3 by metal additives such as Pt, Pd, or Au, via different techniques are under intensive investigations [4, 10, 11, 13, 15, 16, and 25]. It is known that gas sensitivity depends on the high surface area and porosity which are both affected by preparation method. Among various techniques, Sol–gel is a suitable method for preparing nanoparticles. The present work emphasize on hydrogen resistance- sensing properties of Pd:WO_3 films prepared by Sol-gel routs. Films with high homogeneity and low processing temperature are easily made by spinning Pd-W-PTA sols on alumina substrates. We made a series of samples with different morphology to introduce catalyst by electrolysis deposition. Growth and nucleation of Pd particles on the films' surfaces by diluted $PdCl_2$ in water for 2gr/lit was investigated. Resistance-sensing behavior of the prepared films in exposure to diluted hydrogen at operating temperatures of 30 to 350 ^oC by steps of 50 ^oC was measured. Results showed that addition of Pd on the films' surfaces decreased the operating temperature to room temperature but the best performance was at 150 ^0C with increasing sensor's response one hundred times larger than pure film. Also, we obtained good performance as response and recovery times for pure and Pd catalyzed films.

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II. Experimental

A.Thin film Preparation

Peroxopolytungstic acid (P-PTA) sol was prepared by Kudo rout [27]. Five grams of tungsten wire which was cut in 1 cm pieces reacted with 20ml of H_2O_2 (30%).The mixture was stirred at room temperature for 48 hours and all tungsten wire was dissolved. Un-reacted H_2O_2 was removed by using platinum net. Then Ethanol was added and the solution heated at 80 ^oC to evaporate. The sol changes from clear to an orange color. For the activation process, some amorphous films and those which were annealed at 200 ^oC and 500 ^oC were prepared. Pd was introduced by impregnating films in 2gr/lit diluted $PdCl_2$ in water in the presence of HCl for 3 minutes. Then films were dried and annealed at 500 ^oC for 1 hour to be stabilized during gas sensing at high temperatures.

B. *Characterization Techniques*

Film's structures were determined by using XRD, XPS and SEM analysis. The XRD patterns were recorded using a Philips X'pert instrument operating with CuKα radiation (λ=1.54178Å) at 40kV/40mA. Scanning Electron Microscope was used to obtain the SEM images using a Philips XL30 model. The change in resistance towards H_2 was recorded by using a Volt-Amperometric technique. As shown in Fig.1.

Samples with Ti/Au interdigitated electrodes were placed in test chamber, a constant potential was applied and the voltage variation was measured by a voltmeter that was data logged by a computer. The films' temperatures were increased by a heater located on the back of the substrates. We used dry air as a reference gas and Hydrogen as a reducing gas. Sensor response was defined as $S=V_{gas}/V_{air}$ that V_{gas} and V_{air} are the sensor voltage in the presence and absence of gas respectively. The gas sensing performance of the samples to Hydrogen were tested at two gas concentrations of 0.1% and 1% and at operating temperature from 30 ^{o}C to 350 ^{o}C by steps of 50 ^{o}C.

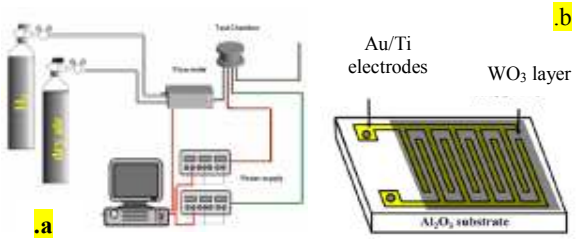

Fig.1 Schematic of gas sensing set up (a) and a typical sensor (b)

III. Results and Discussion

A. *Microstructure Analysis*

Knowledge of surface morphology, crystallite size and films' structure are essential for interpretation of the observed results. The SEM image presented in fig.2 shows growth of three dimensional palladium nanoclusters on the surface.

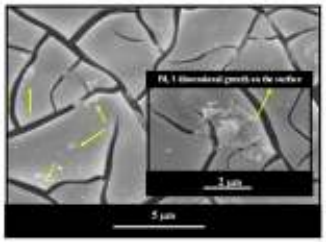

Fig.2 SEM image of Pd electrolysis deposited on WO_3 film

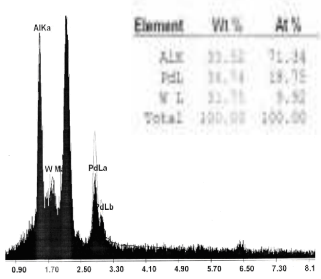

Fig. 3 (a) and (b) shows respectively the XRD patterns of pure and catalyzed films for both the as-prepared (un-annealed) films and heat-treated at 500 ^{o}C. Amorphous $WO_3.H_2O$ structure is observed in all XRD patterns of un-annealed films (Fig. 3a). However heat treatment at 500 ^{o}C results in formation of both nanocrystals of monoclinicWO_3 as presented in Fig. 3(b)

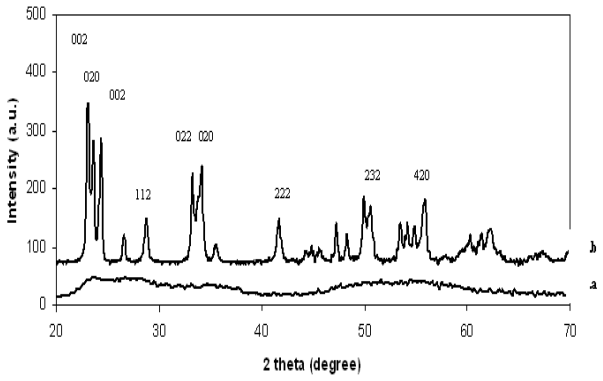

Fig.3 XRD patterns of amorphous (a) and crystallized (b) WO_3 thin films

To find surface composition we performed X-ray Photoelectron Spectroscopy (XPS) experiment. The deconvolution of Pd 3d peaks measured on the annealed film is shown in Fig. 4.

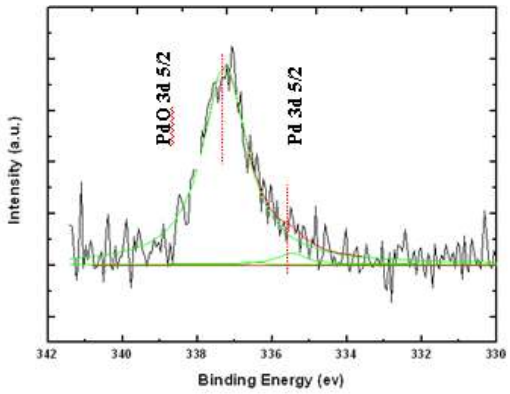

Fig. 4 XPS spectra in the Pd 3d region

It shows the binding energies of oxidized palladium and Pd in metallic state but the metallic Pd has a weak signal.

It confirms that after annealing most of the Pd atoms are in an oxidized state.

B. *Resistance–Temperature Characterization of Samples*

The Pd:WO_3 sensor shows enhanced response to H_2 gas with higher sensitivity compared to the pure one. In Fig.5 the response of pure and catalyzed films to different Hydrogen concentrations at 350 ^oC and a typical variation in electrical conductivity versus time for the annealed film at 200 ^oC are presented.

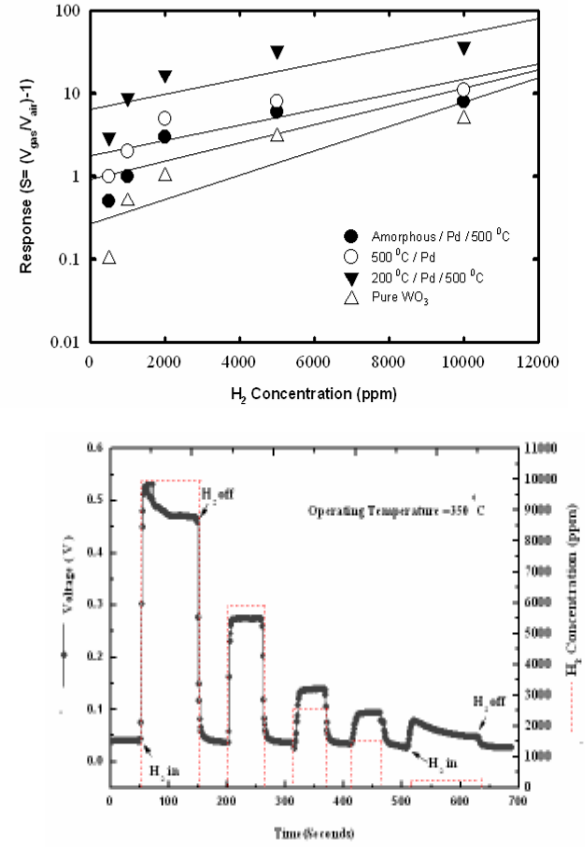

Fig.5 Response of pure and catalyzed films to different Hydrogen concentrations for samples at 350 ^oC (a) and a typical variation in electrical conductivity versus time for annealed film at 200 ^oC (b)

Fig.6 illustrates the response of pure and catalyzed films in Hydrogen concentrations 1% and 0.1% versus operating temperatures from 30 to 350 ^oC. Results showed that each film exhibited a maximum sensitivity at different operating temperature. The best sensing behavior was observed on annealed films at 200 ^oC and operating temperature at 200 ^oC.

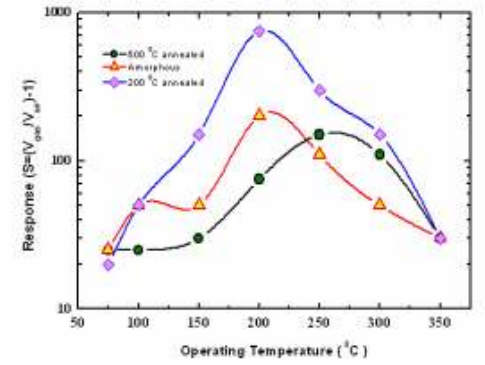

Fig.6 the response of pure and catalyzed films of WO_3 in Hydrogen concentration 0.1% versus operating temperatures

Our results showed surface morphology has a direct role in growth of Pd on the metal oxide surface. In the electrolysis deposition, the chemical reaction between Pd ions and an active surface (WO_3) will be occurred by the following reaction:

$$Pd^{2+}+2e^{-}\rightarrow Pd^{o} \quad (1)$$

Defects and Oxygen vacancies in metal Oxides play an important role in charge exchange with metal ions. In this work, amorphous film prepared by sol-gel route contains $WO_3.2H_2O$ nanoparticles with many defects and vacancies. Annealing the films at 200^0C can remove water but defects and vacancies still exist and higher annealing temperatures like 500^oC would reduce these defects. Consequently, we can observe more Pd growth on the amorphous and 200 ^oC annealed films in the form of nanoclusters as is shown in fig.2. This is due to large concentration of defects on these films In fact the amorphous films have large amount of water in their structure which produces more point defects during impregnation in catalyst solution. In accordance to SEM and resistance-sensing results, these structural defects cause more growth of Pd nanoclusters on the surface in compare to annealed samples at 500 ^oC. Also increase in $PdCl_2$ concentrations from 0.2gr/lit to 2gr/lit leads to more accumulation of Pd particles on the surface.

II. Conclusion

Electrolysis technique is a useful method for introducing palladium on metal oxides surface. According to our SEM results, dispersion and growth of the Pd particles on the surface of samples are affected strongly by the film's morphology. Increasing the Pd-salt concentration, cause an increase in the size of Pd particles and make higher agglomerations of these clusters in some places. The gas sensing performance of the films to Hydrogen is directly related to the features of Pd growth. The 200^oC annealed film

showed best performance because of response at lower operating temperature which is desirable for commercial application.

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