# 34. Hydrogen Gas Sensor Based On Nanocrystalline Titanium Dioxide Thin Film Prepared By Simple Spray Pyrolysis Technique

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**Abstract**

In the Present work the spray pyrolysis technique was employed to prepare nanocrystalline $TiO_2$ thin film. Their gas sensing properties are strongly dependent on deposition technique. To prepare nanocrystalline $TiO_2$ thin film by using solution of AR grade Titanium chloride ($TiCl_3$, 0.01 M). The solution was sprayed on quartz substrate heated at $350^0$C temperature to obtain the film. This thin film was annealed for a one hours at $550^0$C. As prepared thin film was characterized by X-ray diffraction, Microstructure study was conducted using Transmission Electron Microscopy and Optical properties was studied using U-V Spectroscopy. The sensing performance of this thin film was tested for various gases such as LPG, $H_2$, $CO_2$, Ethanol, $NH_3$ and $Cl_2$ (100 ppm). Gas response, selectivity, response and recovery time of the sensor were measured and presented.

**Keywords:** Spray pyrolysis techniques, $TiO_2$ thin films, Hydrogen gas sensor.

## 1. Introduction

Over the last few years a great attention has been focused on the titanium dioxide ($TiO_2$) thin films because its excellent materials in many applications such as in the field of sensors, antireflection coatings, gas sensors[1], solar cells[2] and photocatalysis [3,4]. There are many methods that can be used to prepare $TiO_2$ thin films with desired properties including sol-gel [4-

7], sputtering [8], anodic oxidation [9-14], pulsed laser deposition (PLD) [15] and spray pyrolysis [1-3, 16-17]. Of all the afore-mentioned thin film fabrication methods, spray pyrolysis is widely used because of its simplicity, cheap chemical deposition procedure, allowing the growth of rough-surface films at atmospheric pressure, on large area.

Hydrogen gas is tasteless, colorless and odorless so it cannot be detected by human beings. The low ignition energy and wide flammable range makes it easy inflammable and explosive. Therefore rapid and accurate hydrogen detection is necessary during the production, storage and use of hydrogen and it is also essential for monitoring/controlling the hydrogen concentration of nuclear reactors, coal mines and semiconductor manufacturing, etc [18].

## 2. Experimental

### 2.1 Preparation of pure $TiO_2$ thin film

The spray pyrolysis technique was employed to prepare $TiO_2$ thin film. Aqueous solution of Titanium chloride was used as precursor ($TiCl_3 \cdot 6H_2O$, 99.9% pure,Merck made, Germany) with concentrations of 0.01 M, were prepared in double distilled water.The solution was sprayed onto glass substrate heated at $350^0C$ to obtain the film. This thin film was fired for a one hour at $550^0C$ and termed as S.

## 3. Materials characterizations

The structural analysis of nanocrystalline $TiO_2$ thin films was carried out by XRD (Rigaku DMAX 2500) with CuKα radiation at a wavelength of 1.5418 Å. Electron diffraction patterns of nanocrystalline $TiO_2$ thin films were obtained using a Transmission Electron Microscopy [Philips, CM 200 (200 KV HT)]. A UV-Visible spectrophotometer (Shimadzu 2450 UV-VIS) was used to study the optical properties of nanocrystalline $TiO_2$ thin film. The thickness and roughness of thin film was measured by using Surface Profiler [AMBIOS Tech. (USA) XP-I].

### 3.1 Thickness and roughness determination of $TiO_2$ thin films

The thickness and roughness of thin film was measured by using Surface Profiler (AMBIOS Tech. (USA) XP-I) having vertical resolution of 1.5Å, Lateral resolution of 100 nm and lateral length of 200 nm.  From this, thickness of nanocrystalline $TiO_2$ sample is 223.8nm and roughness of sample $TiO_2$ is 33.3nm.

### 3.2 Structural properties: X-ray diffraction studies

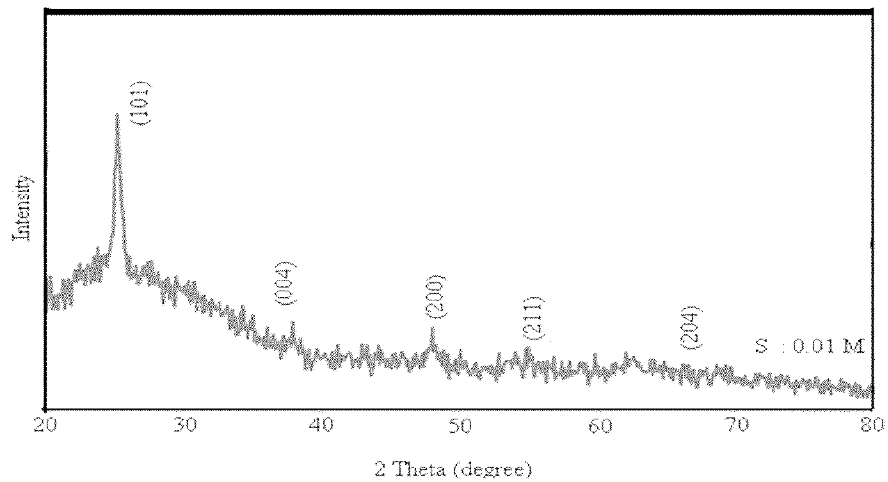



**Figure 1:** X-ray diffraction spectra of sample S

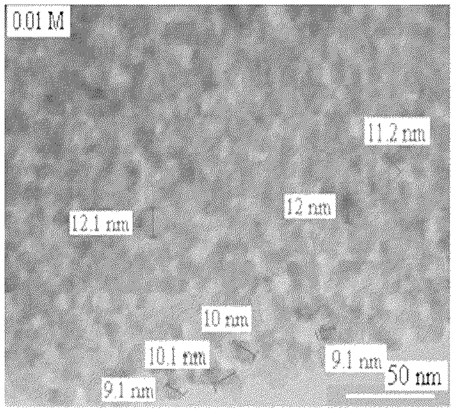
Figure 1 shows XRD spectra of sample S. The observed "d" values of $TiO_2$ films confirmed that the deposited films are of $TiO_2$ anatase phase with tetragonal structure matched well with the ASTM data book [19]. In the XRD pattern, the (101) peak has the most distinct reflection. So, the mean crystalline size is calculated with the line broadening of the (101) reflection using well known Scherrer Eq. (1)

$$d = 0.9\,\lambda / \beta \cos\theta \qquad (1)$$

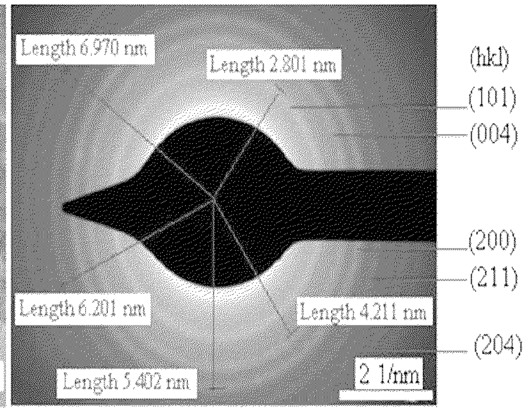
Where, d is crystallite size, $\beta$ is the full width at half maxima in radians and $\lambda$ the wavelength of X-ray (1.5418 Å). The crystallite size was observed to be 9.24 nm.

### 3.3 Microstructure and electron diffraction using TEM

Figure 2 (a) shows the Transmission Electron Micrograph [CM 200 Philips (200 kV HT)] of powders obtained by scratching the thin film sample S and powder was dispersed in ethanol. TEM uses copper grid to hold the powder. The sample particles on the grid were scanned in all the zones before the picture was taken. Figure 2 (a) shows that the grains are spherical or ellipsoidal in nature with an average grain size of 10.52 nm. Fig. 2 (b) shows the electron diffraction patterns of S. The electron diffraction patterns show clear and continuous ring patterns revealing their polycrystalline structure. Five fringe patterns corresponding to planes: (1 0 1), (0 0 4), (2 0 0), (2 1 1) and (2 0 4) are consistent with the peaks observed in XRD patterns. XRD and TEM studies confirmed pure tetragonal structure of $TiO_2$ as evidenced from figure 1 and figure 2 respectively. Table 2 show the comparison of grain size from Transmission Electron Micrograph and X-ray Diffraction.




(a)




(b)

Figure (a): TEM image of sample S

Figure (b): Electron diffraction image of sample S

Table 2: Grain size calculated from XRD and TEM.

| Sample | Grain size calculated from XRD(nm) | Grain size calculated from TEM (nm) |
|---|---|---|
| S | 9.24 | 10.52 |

### 3.4 Optical absorption

Figure 3 show the variation of absorbance with wavelength of nanocrystalline $TiO_2$ thin films in the range of 300-600 nm. The band gap energy of the samples was calculated from the absorption edges of the spectra [20]. The band gap was observed to be 3.28 ev.

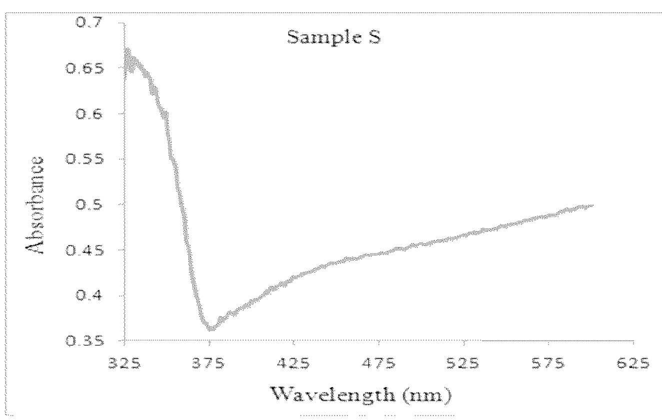



**Figure 3:** Absorption spectra of samples S

## 4. Sensing performance of pure $TiO_2$ thin films

### 4.1 Gas sensing performance of thin film resistors

The thin film sensors mounted in static gas sensing system were tested on exposure of ethanol, carbon dioxide, LPG, ammonia, chlorine and hydrogen. Values of currents before and after exposure of gas were measured and gas responses at various operating temperatures were determined.

### 4.2 Measurement of gas response and selectivity

Gas response (S) is defined as the ratio of the change in conductance of the sensor on exposure to the target gas to the original conductance in air. The relation for S is as:

$$S = (G_g - G_a) / G_a$$

where, $G_a$ and $G_g$ are the conductance of sensor in air and in a target gas medium, respectively.

Selectivity or specificity is defined as the ability of a sensor to respond to a certain gas in the presence of other gases.

### 4.3 Variation of gas response with operating temperature for different gases

Figure 4 shows the variation of gas responses with operating temperature. It is clear from the figure 4 that the gas response increases with operating temperature, reaches to maximum [for $H_2$ (S=22) at 250$^0$C for 100ppm] and falls with further increase in operating temperature. Sensor S is most sensitive to $H_2$ at 250$^0$C.

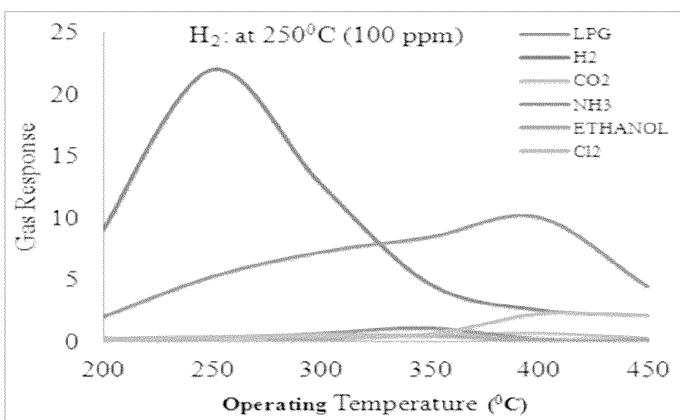



**Figure 4:** Variation of gas responses with operating temperature.

## 5. Discussion

It is well known that oxygen molecules are adsorbed on the surface of $TiO_2$ to form $O_2$, O, and $O^2$ ions by abstracting electrons from the conduction band of $TiO_2$ depending on temperature. The oxygen species are $O_2$ molecules below $100^0$C, $O_2^-$ between 100 and $300^0$C, and $O^{2-}$ above $300^0$C [21].

$$H_{2\,(ads)} + O^-_{\ (ads)} \rightarrow H_2O_{\ (gas)} + e^- \qquad (2)$$

When the $TiO_2$ thin films are exposed to $H_2$ gas, the $H_2$ gas reacts with the adsorbed $O^-$ ions on the surface of $TiO_2$ thin films according to equation (4.6). Then, electrons are returned back to the films. Increase of electrons decreases the resistance of the $TiO_2$ thin films and conductivity increases upon exposure to $H_2$.

**6. Conclusions**

- The grain sizes of sample S is calculated from XRD match well with the grain sizes observed from TEM.
- Nanocrystalline $TiO_2$ thin films were observed to be sensitive to hydrogen at $250^0$C.
- Nanocrystalline nature was observed to be useful in gas sensing.

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