Sputtering Pressure Dependent Structural, Optical and Hydrophobic Properties of DC sputtered Pd/WO_3 thin films for Hydrogen Sensing Application

Sonam Jain[1, 2], Amit Sanger[1], Ramesh Chandra[1]*

[1]*Nanoscience Laboratory, Institute Instrumentation Centre, Indian Institute of Technology Roorkee, Roorkee-247667, India*

[2]*Centre of Nanotechnology, Indian Institute of Technology Roorkee, Roorkee-247667, India*

ABSTRACT

Hydrogen is known as one of the clean and efficient energy source with a potential to be used as a fuel for industrial applications. The present study investigates the influence of Sputtering pressure on hydrogen sensing response of Pd/WO_3nanostructured thin films. The bilayer Pd/WO_3 thin films were prepared by Dc magnetron sputtering on the glass and silicon substrates. The thin films were characterized using X-ray diffraction (XRD),UV-Vis-NIR spectrophotometer, Atomic force microscope (AFM) and Contact angle measurement. The crystallite sizewas found to increase with increase in sputtering pressure. The wettability of the samples was found to increase with increase in pressure. The value of roughness obtained from AFM showed the similar trend. The temperature dependent hydrogen response was studied in temperature range from 50-150^{o}C.The as deposited WO_3 samples were found to be transparent however the transparency decreases on hydrogen exposure due to the formation of blue tungsten bronze. The effect of water vapor during dehydrogenation was studied. The change in sensing response of the thin film was correlated with the hydrophobicity of the samples. Stability of the samples was observed to be retained after hydrogenation & dehydrogenation cycle. The response time of around 1sec for the thin film prepared at 20 mtorr is reported.

Keywords: Sputtering, Metal oxide, Porosity, Hydrophobicity, Hydrogen Sensing.

1. INTRODUCTION

Hydrogen is considered as a future fuel for storing and transporting the energy as it can be easily transformed into electrical energy and vice-versa with a greater degree of efficiency (55-70%) [1].Hydrogen has a high standard heat of combustion of 141.9 kJ/g. Hydrogen is a clean energy resource producing a benign oxidation product-water. Currently, hydrogen is used as a popular process gas in petroleum refining, chemical and food industries, chlorine production, monitoring of nuclear waste, fuel cells etc. However, effective and fast hydrogen gas detection technologies are crucial for large scale hydrogen based applications.

Tungsten oxide is a promising hydrogen gas sensing material due to its chemical stability and a very high diffusion coefficient [2]. It is an indirect band gap n-type semiconductor with reportedband gap in the range from 2.6-3.1 eV [3]. Till date WO_3 thin films have been prepared by several methods[4] including vacuum evaporation, sol-gel, Pulse laser deposition(PLD), sputtering. Sputtering is used in our study for the WO_3 thin film preparation due to its ability to produce uniform and crystalline films. Later is considered as a novel method for thin film deposition as it allows to control the structural properties by varying sputtering parameters [5].

In this study, we explain the hydrogen sensing mechanism of bilayer Pd/WO_3 thin films prepared by Dc magnetron sputtering. The influence of sputtering pressure on structural, optical and hydrophobic properties was studied and henceforth the change in hydrogen sensing performance of as-prepared samples is reported.

2. EXPERIMENTAL DETAILS

WO_3 and bilayer Pd/WO_3 nanostructured thin films were deposited on glass and silicon substrates by Dc magnetron sputtering using 25mm diameter and 3mm thick tungsten (99.96% purity) and Pd (99.95% purity) targets. High purity inert gas (99.99% pure Ar) and reactive gas (99.99% pure O_2) were used for sputtering. The substrate were initially cleaned by rinsing in ultrasonic bath of acetone for 10 min and then blown dry in air to remove surface contaminants. The sputtering pressure was varied from 5 to 20mTorr, keeping all other parameters constant. The target was pre-sputtered for 5 min to remove negative ions on the surface of target. Afterwards, Pd was deposited on the WO_3film surface for5sec sputtering at 30W. Table1 lists the deposition parameters used:

Table 1. Deposition parameters for WO_3 thin films

Sputtering Parameters -	
Target	Tungsten(W)
Base Pressure	6x10-6 torr
Working Pressure	5-20 mtorr
Deposition time	5 min
Power	100W
Substrate Temperature	300oC
Target-substrate distance	50mm
Sputtering Gases	Ar,O2
Substrate	Glass, Silicon

3. RESULTS & DISCUSSIONS

The XRD patterns of WO_3 nanostructured thin films prepared at varying sputtering pressure are shown in Fig.1. The dominant peak obtained at 28^o is attributed to the It(002) plane of monoclinic phase of WO_3. Monoclinic phase can exist at room temperature, hence it is acknowledged as a stable phase [3]. The particle size of the thin films increases and hence the crystallinity of the thin films improved as the sputtering pressure is increased from 10-20 mtorr. The particle size can be estimated from Scherrer's formula[6] following in equation(1):

$t=0.9\ \lambda/(\beta\cos\theta)$(1)where, λ and θ are the wavelength of Cuk_α(1.542 A□) and Bragg's angle respectively, $\beta$is FWHM (Full Width Half Maximum) of the dominant peak.

The variation of crystallite size 't' with sputtering pressure can be explained on the basis of relationship between mean free path , molecular diameter of sputtering gas and distance between target and substrate inside sputtering chamber as given in equation (2) :

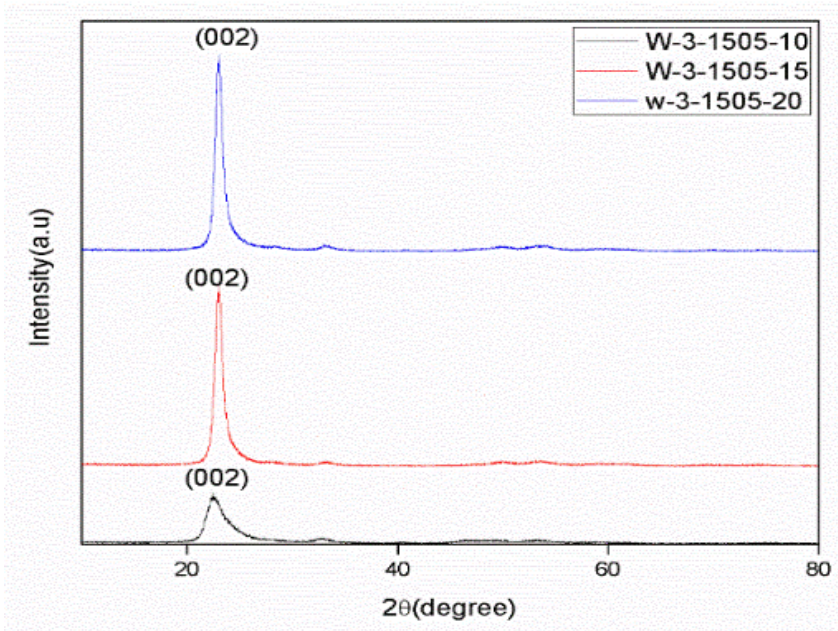
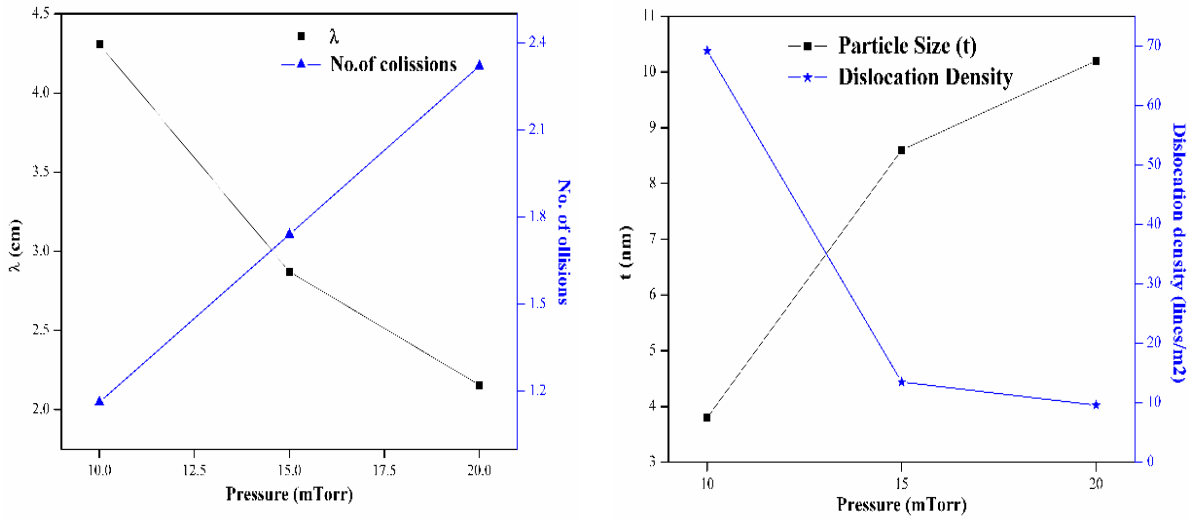


Fig.1. XRD patterns of WO3 thin films at different sputtering pressure

$\lambda = kT/(\sqrt{2}\pi P\gamma^2)$(2)

where, λ is the mean free path, γ is the molecular diameter of sputtering gas, P is pressure of sputtering gas.



(a) (b)

Fig.2 (a) variation of mean free path and no. of collisions with pressure, (b) dependence ofparticle size and dislocation density with sputtering pressure.

The variation of dislocation density with the sputtering pressure is shown in Fig.2. Dislocation density gives the number of crystal defects in a film. Dislocation density (D.D) can be estimated using the following relation given in equation (3):

$$D.D = 1/t^2 \text{ lines/m}^2 \quad (3)$$

Dislocation density was observed to be minimum at 20mtorr indicating minimum number of crystal defects at that particular pressure.

Optical properties of the thin films were observed to be strongly dependent on the sputtering pressure. The optical transmittance spectra of WO3 thin films for different sputtering pressure is as shown in fig.6. The optical transmittance spectra of the thin film increases from 40 % to 92% at 500nm with increase in sputtering pressure to 20mtorr. At lower sputtering pressure, oxygen is unable to deposit with tungsten and hence films formed at lower pressure exhibited a lower optical transmittance. On the other hand, both oxygen and tungsten gets deposited forming nearly transparent films with higher optical transmittance (90%) at higher sputtering pressure. On depositing Pd onto WO_3 thin films a considerable decrease in transmittance spectra was observed.

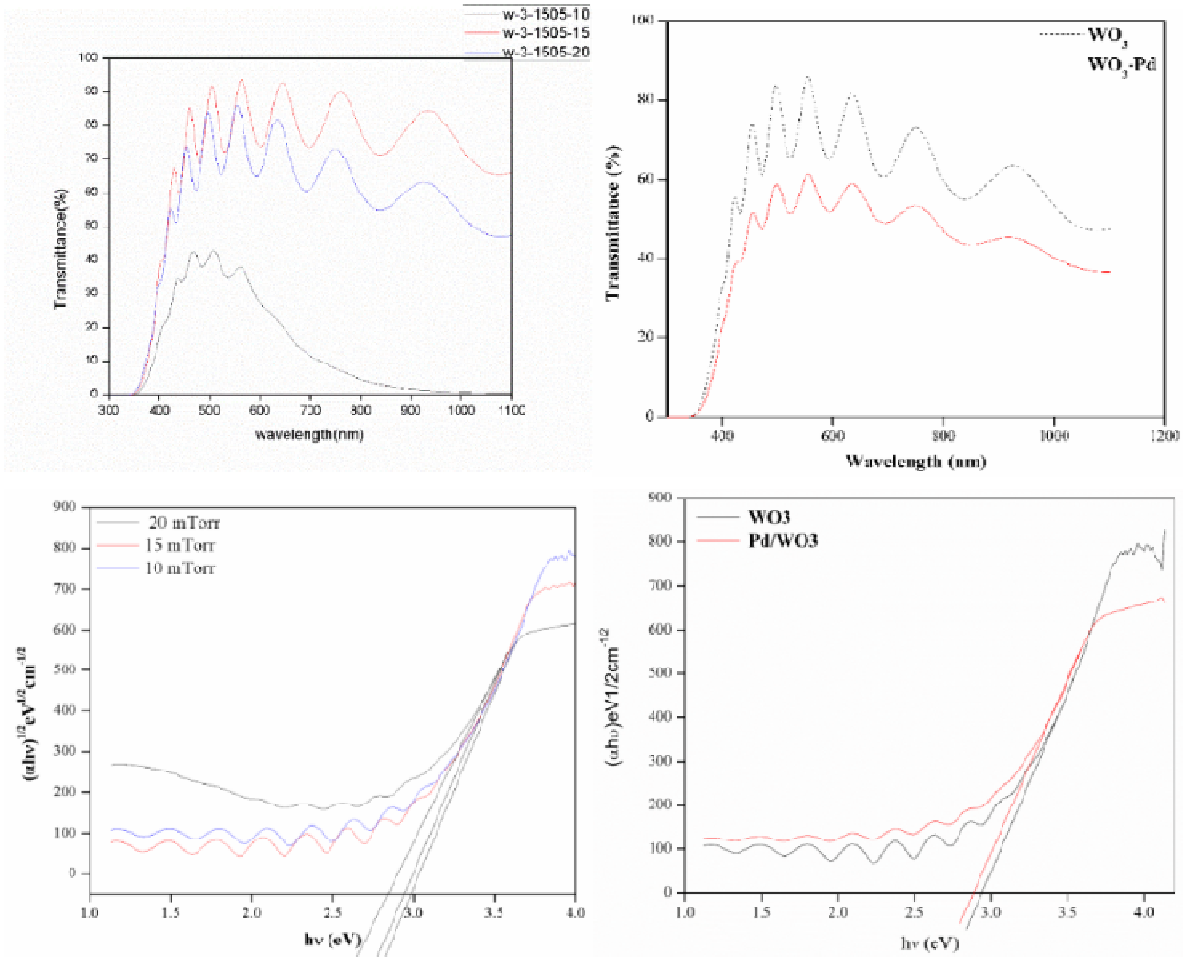


Fig.3 (a) and (c) show the transmittance and energy band gap at different sputtering pressure, Fig. (b) and (d) shows the transmittance and band gap for sample deposited at 20 mtorr.

The optical energy band gap is calculated using Tauc's relation [7]:

$$(\alpha h\nu)^m = \beta(h\nu - Eg) \quad (4)$$

where, hν is theincident photon energy and Eg is the optical band gap of the material. α is absorption coefficient, β is a transition probability parameter. Parameter m is transition coefficientand corresponds to ½ and 2 for indirect and direct band gap respectively. The band gap of the films decreased from3 to 2.7 eV with increase in sputtering pressure from 10mtorr to 20 mtorr. The decrease in band gap with pressure is due to the fact that Pd occupies the interstitial

layers between the valence band and conduction band thereby decreasing band gap.The obtained band gap values are in close agreement with those reported in literature.

The *refractive index* of the thin films can be determined using swanepoel's envelope method [8]:

$$n= [N+(N^2-n_o^2n_1^2)^{1/2}]^{1/2} \quad (5)$$

where, $N=(n_o^2+n_1^2)/2 + [2n_on_1 (Tmax-Tmin)/(Tmax*Tmin)]$; n_o and n_1 are the refractive indices of air and substrate respectively.

Fig.4 shows the dependence of refractive index with sputtering pressure. The refractive index of the thin films decreased to 2.18 at 20 mtorr. The decrease in refractive index may be attributed to the decrease in the packing density of the thin films formed at higher sputtering pressure.

Fig.5 shows the *3-D AFM micrographs* of Pd/WO_3 thin films at different sputtering pressure. It is evident from the micrographs that the roughness of the films increases with sputtering pressure. The variation in the roughness of the films can be attributed to the increase in crystallite size with sputtering pressure which in turn increases the roughness of the films.

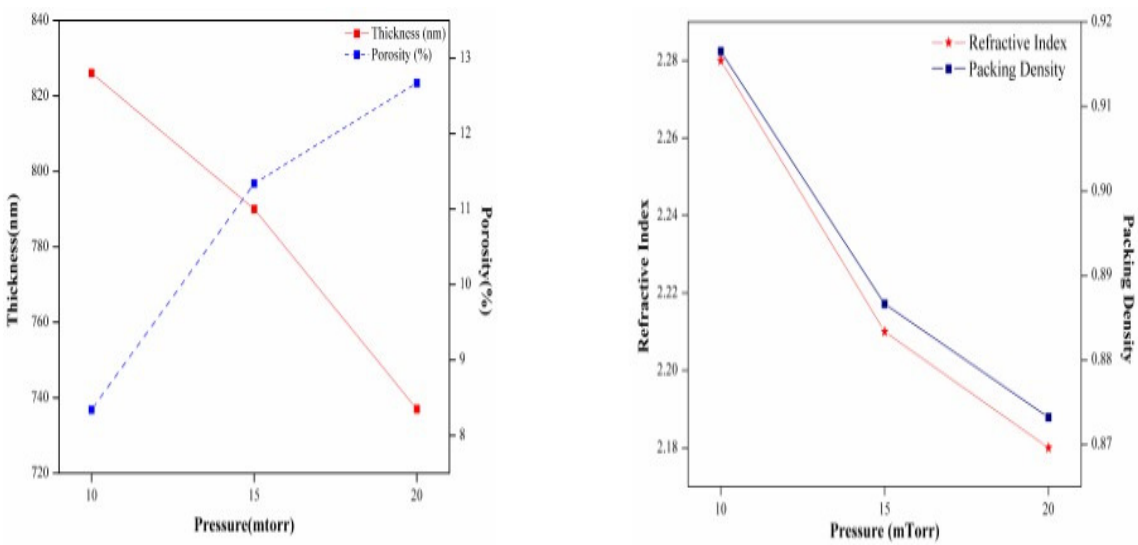


Fig. 4(a) variation of thickness and porosity with pressure, (b) variation of refractive index and packing density with pressure.

Hydrophobicity of the bilayer Pd/WO_3 thin films was calculated using contact angle measurement.

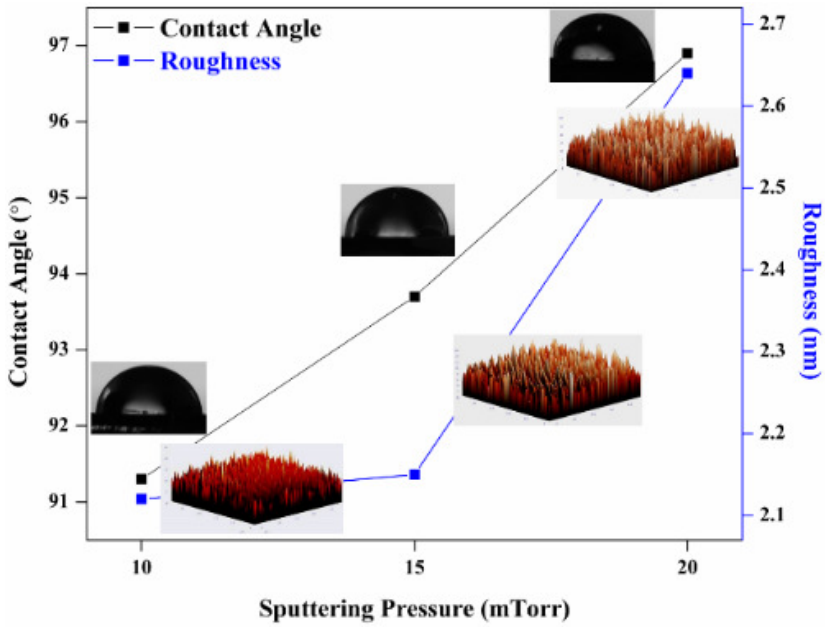


Fig: 5 Variation of Contact angle and Roughness with Sputtering Pressure.

A surface is considered as hydrophobic if $\theta>90^{o}$[9].The variation of hydrophobicity (contact angle) and roughness of the film surface with sputtering pressure is shown in fig.5. Both are observed to show the same trend. The reason for this may be attributed to the inability of the liquid to fill cavities at the rough surface and thereby creating air pockets at solid-air-liquid interface.

4. HYDROGEN RESPONSE OF PD/WO_3 THIN FILMS:

The sensing response of bilayer Pd/WO_3 thin film is observed using resistance change on hydrogenation. Fig.6 shows the variation of resistance of Pd/WO_3 bilayer films with time during hydrogenation/dehydrogenation cycle. It has been observed that the sensor response rose considerably on increasing sputtering pressure. The reason may be attributed to reducing the grain size and increasing porosity with increasing pressure.*Sensor Response(S.R)* can be estimated using $(R_o-R_g)/R_g$, where, R_o and R_g are the resistances of the Pd/WO_3 films in air and in presence of hydrogen respectively. The response time of around 1sec is reported for the film prepared at 20 mtorr.In air, Oxygen chemisorbs on the surface of the WO_3 thin films and trap free electrons from the conduction band of WO_3 due to their high electron affinity and results in an electron depletion region. This build up a large resistance in that area due to lack of carriers and the potential barrier induced inhibits the carrier mobility [10].

$$O_2 + 2e^- \quad 2O^-(ads) \qquad \Longrightarrow \qquad (7)$$

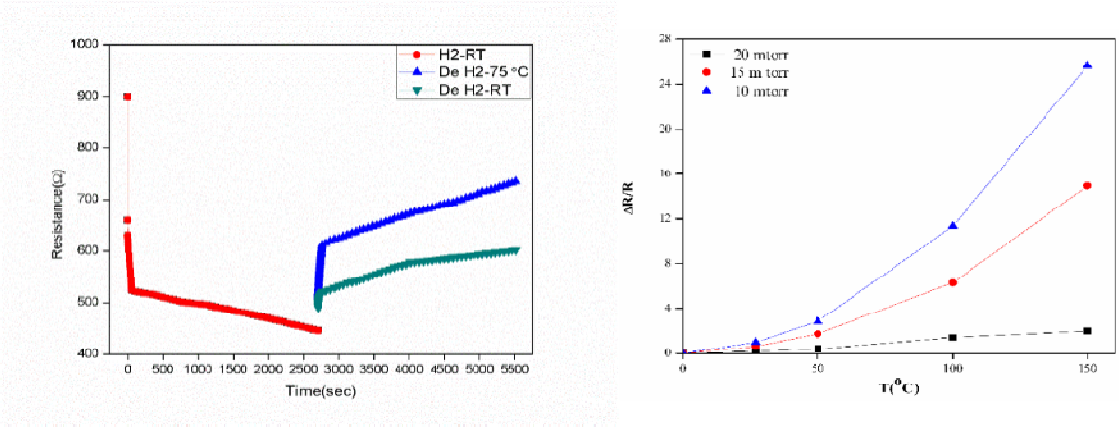


Fig. 6 (a) hydrogenation/de-hydrogenation for sample prepared at 20 mtorr, (b) sensor response as a function of temperature.

However, when H_2 is introduced it reacts with the oxygen species. Catalyst dissociates the H_2 molecules to H atoms which reacts with tungsten oxide to form blue tungsten bronze[11]. Electrons released in the process are given back to the semiconductor which lowers the potential barrier and allows the current to flow thereby increasing conductivity.

$$2H\square\ (\text{ad-atoms}) + O^{-}\ (\text{ads}) \rightarrow H_2O + e^{-} \qquad (8)$$

$$xH\square\ (\text{ads}) + WO_3HxWO_3 \rightarrow \qquad (9)$$

5. CONCLUSION

Nano-structured bilayer Pd/WO3 thin films were fabricated using DC magnetron sputtering at varying sputtering pressure. The hydrophobic, structural and optical properties of the thin films were investigated. All the samples prepared were observed to show a stable monoclinic phase. The porosity (12.67%), roughness (2.64nm) and contact angle (96.9^{o}) were found to be maximum at 20mtorr. The sensor response also showed highest value at 20mtorr. The reason for this may be attributed to the fact that the high porosity and small grain size facilitates the diffusion of the hydrogen within thin film lattice, thereby considerably increasing the sensor response. Studies show that metal oxide Pd/WO3 thin films prepared at 20mtorr proves to be a fast and stable hydrogen sensing material.

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