Applied Innovative Research
Vol. 1, June 2019, pp. 96-100

Hydrogen induced resistance and optical transmittance of pulsed laser deposited Pd/Mg thin films

Yogendra K Gautam[a]*, Ashwani Kumar[b], Anit K Ambedkar[a], Vipin Kumar[a] & Beer Pal Singh[a]
[a]Smart Materials and Sensor Laboratory, Department of Physics, CCS University campus Meerut, Meerut 250 004, India
[b]Nanoscience Laboratory, Institute Instrumentation Centre, Indian Institute of Technology Roorkee, Roorkee 247 667, India

Received 31 May 2019; accepted 19 June 2019

The hydrogen detection is an important issue for the societal acceptance of H_2 as energy carrier. In present research work, we have investigated hydrogen sensing and optical properties of Pd/Mg thin films on glass substrate deposited by pulsed laser (PL). As-deposited thin films have been exposed (hydrogenation) to H_2 gas (2 bar) at room temperature in a hydrogenation unit. Hydrogenated and dehydrogenated (at different temperatures) samples have been characterized using X-ray diffractometer (XRD), field-emission scanning electron microscopy (FE-SEM), UV-Vis-NIR spectrophotometer, atomic force microscopy (AFM). XRD results confirm the formation of hydride (MgH_2) tetragonal phase upon hydrogenation of Pd/Mg films. Hydrogen induced resistance response of Pd/Mg films has been measured in-situ during hydrogenation/dehydrogenation process by using two- probe electrical method. The response time (sensitivity) of Pd/Mg films for hydrogen gas is ~ 60 s at room temperature. The study of optical transmittance of hydrogenated Pd/Mg films indicates their switchable mirror behavior.

Keywords: Palladium, MgH_2 thin film, Hydrogen sensor, Pulsed laser deposition, Electrical measurement

1 Introduction

Hydrogen is energy carriers like petroleum, natural gas or coal, which is used in fuel cell and provides electrical energy with high efficiencies (50-60 %) without any pollutants[1]. This also reduces the greenhouse and other harmful emissions from stationary and mobile stores[2]. Hydrogen is colorless, odorless and tasteless flammable gas so it cannot be detected by human sense. Therefore, rapid and accurate hydrogen detection is necessary during the production, storage and use of hydrogen[3-5]. Now –a - days, traditional hydrogen detectors use metal oxide-semiconductors but all have high operation temperature and high cost[6-13]. Hence, the detection of H_2 gas leaks is a challenging task for developing of hydrogen economy. Many researchers are working to overcome the problems with development of suitable hydrogen gas sensors[14-17]. Good sensitivity (response time ~ 230 sec) were observed for electrochemically grown palladium (Pd) nanoparticles compare to sputter deposited Pd thin films (sensing time ~ 300 sec) for 2.5 % H_2 concentration[18]. The response time of Pd thin film of lower thickness (100 nm) was measured which is ~ 130 and 480 s in 1 % and 2 % of H_2 concentration in ambient, respectively[19]. It was observed that Pd can be used as sensing material for low H_2 concentration at room temperature but palladium is a costly and not suitable of higher H_2 concentration. To overcome this difficulty, the use of magnesium (Mg) thin film with very thin (3-5 nm) Pd-capping layer can be a cost effective H_2 sensing material as compare to pure Pd[17].

It was observed that hydrogen is absorbed by magnetron sputtered Pd-doped Mg thin films within few minutes at room temperature under low H_2 pressure[20] (0.5 bars). Hydrogen sensing property of Mg-Pd alloy films were reported for different concentrations of hydrogen[21]. A study on pulse like hydrogen sensing property of Pd nanoparticle layers has been reported by Khanuja *et al*[22]. Tang *et al*. proposed new methods to improve H_2 sensing properties of Pd/Mg-Ni films[23]. The optical properties of Pd-capped metallic films (magnesium, lanthanum, yttrium etc.) can be changed reversibly between reflective and transparent states upon hydrogenation/dehydrogenation process[17-23]. Therefore, much attention is being paid world widely to develop these coatings for the applications in optical mirrors. These mirrors have the potential to control the optical transmittance or optical reflectance after hydrogen inclusion. They are of great interest as the switchable glazing in smart windows, and thus can contribute in saving energy for air conditioning etc[24]. A visible optical change along with Pd/Mg thin films/multilayers in

*Corresponding author (E-mail: ykg.iitr@gmail.com)

hydrogen partial pressure (2- 4×10^3 Pa) has been reported[24]. An electrical and optical change in Pd-capped Mg, i.e., Pd/Mg after is the key to develop a hydrogen sensor with high sensitivity and switchable mirror. In the present work, we have investigated hydrogen sensing and optical properties of Pd/Mg thin films on glass substrate.

2 Experimental Details

2.1 Synthesis of Pd/Mg thin films

Palladium-capped magnesium (Pd/Mg) thin films was deposited on glass substrate by pulsed laser deposition (PLD) technique using Pd (99.95% purity) and Mg (99.98% purity) targets of 2-inch diameter and 3 mm thickness. A krypton fluoride (KrF) excimer laser (Lambda Physik model Compex Pro 201) was used with 248 nm wavelength and energy of 0.2J per pulse[14, 17]. The deposition parameters are given in Table 1.

2.2 Characterization details

The thickness of the Pd/Mg thin films was estimated from cross-sectional view using field emission scanning electron microscopy (FE-SEM) (Carl Zeiss, Ultra Plus). XRD spectra of as-deposited, hydrogenated and dehydrogenated Pd/Mg thin films were recorded using CuK_α radiation in glazing X-ray diffractometer (Bruker AXS, D8 Advance). Optical transmittance measurements of as-deposited and hydrogenated Pd/Mg thin films were carried out in the wavelength range (3-30×10^2 nm) using UV spectrophotometer (Varian, Cary 5000). Surface morphology of the samples was investigated using AFM (NT-MDT, Ntegra). The estimated thickness value of as-deposited Pd/Mg films is ~ 160 nm (Fig. 1).

3 Results and Discussion

3.1 Structural and morphological study

The XRD patterns of as-deposited, after hydrogen absorption (hydrogenated) and desorption (dehydrogenated) Pd/Mg thin film are shown in Fig. 2. The as-deposited films are found polycrystalline in nature and has major diffraction peaks corresponding to a hexagonal closed packed (hcp) structure of Mg (002) at 34.36° and Mg (101) at 36.52°, respectively[25]. We have not observed any peak for Pd because it was deposited for very short time (thickness ~ 3-5 nm). For hydrogenated (2 bar H_2, at room temperature) sample, the dominant peak of tetragonal α-MgH_2 (200) is observed[26] at 38.09°. The Peaks at 28.37° and 44.14° are also identified as α-MgH_2 (110) and α-MgH_2 (210), respectively. This indicates that hydrogen reacts with Mg to form MgH_2 and a phase transformation from hcp-structure of Mg to the rutile structure of MgH_2 occurs.

In hydride formation process, the Pd capping layer on the surface of Mg film works as catalyst to

Table 1 — Experimental parameters used to deposition of Pd/ Mg thin films.

Target	Pd, Mg
Substrate	Glass
Target-substrate distance	4.0(cm)
Base pressure	4×10^{-6} (Torr)
Laser energy per pulse	400(mJ)
No. of shots	2000(Pd), 25000(Mg)
Substrate temperature	100(°C)

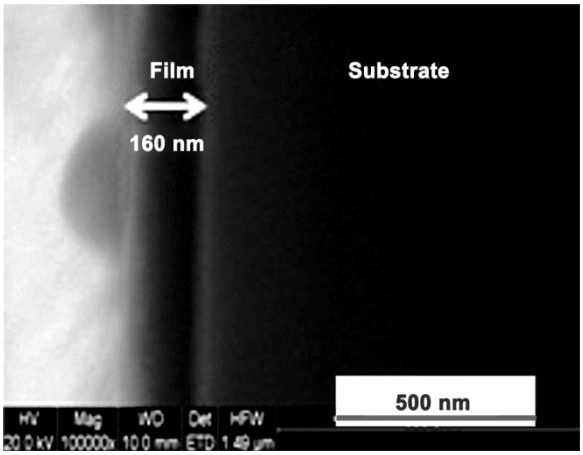

Fig. 1 — FE-SEM cross-section image of as-deposited Pd/Mg films on glass substrates.

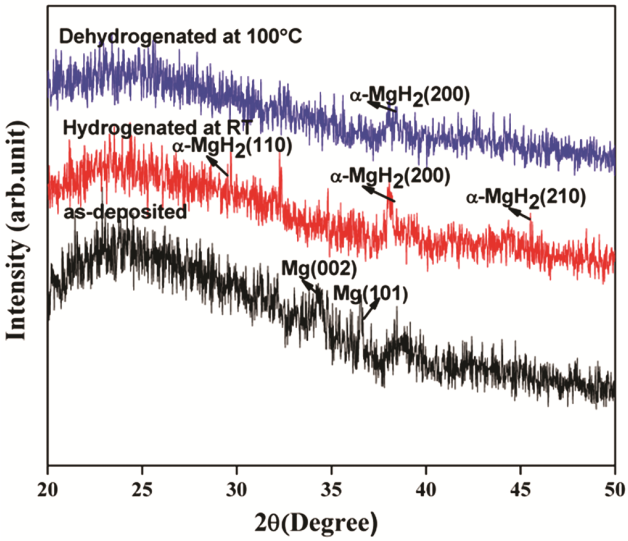

Fig. 2 — XRD pattern of as-deposited, hydrogenated and dehydrogenated Pd/Mg films on glass.

dissociate the hydrogen molecules into hydrogen atoms which in-turn diffuse into Mg and form MgH_2. Intensity of MgH_2 hydride peaks is low, small peel-off effect has been noticed due to weak adhesion of films on the glass substrate[27]. The adhesive force between the substrate and the Mg film is larger than that between Mg and Pd film[28]. In dehydrogenated sample, the presence of hydride peak indicates that complete hydrogen desorption does not occur in the given conditions (100 °C for 30 min). It will take time more (> 30 min) to remove all hydrogen from Mg. This is because of higher desorption temperature for Mg film of thickness[29] >100 nm.

The 2D and 3D AFM images (scan area 2×2 μm) of the topography of as-deposited and hydrogenated samples are shown in Figs. 3 and 4, respectively.

Figure 3 shows very smooth, uniform and pin-hole free and mirror-like surface morphology of as-deposited Pd/Mg thin film. The average grain size has been measured using AFM and it has been found to be ~ 20 nm. The rms surface roughness of the samples is ~ 5 nm.

It has been measured that, the grain size and rms surface roughness is increased in hydrogenated Pd/Mg thin film. The measured value of grain size is ~60 nm and rms surface roughness is ~14 nm,

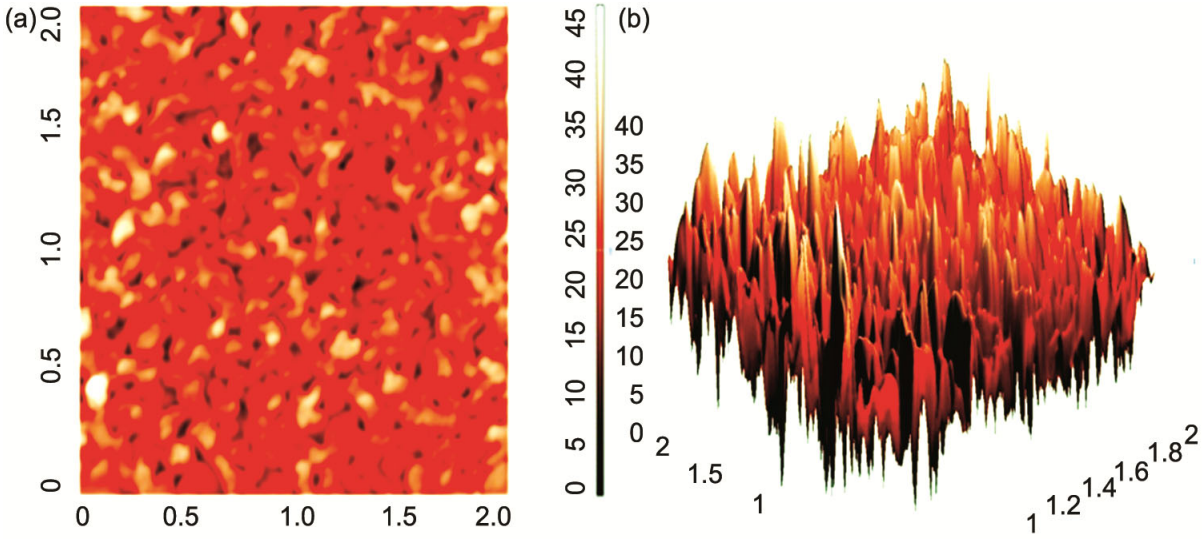

Fig. 3 — 2D and 3D AFM images of as-deposited Pd/Mg thin films.

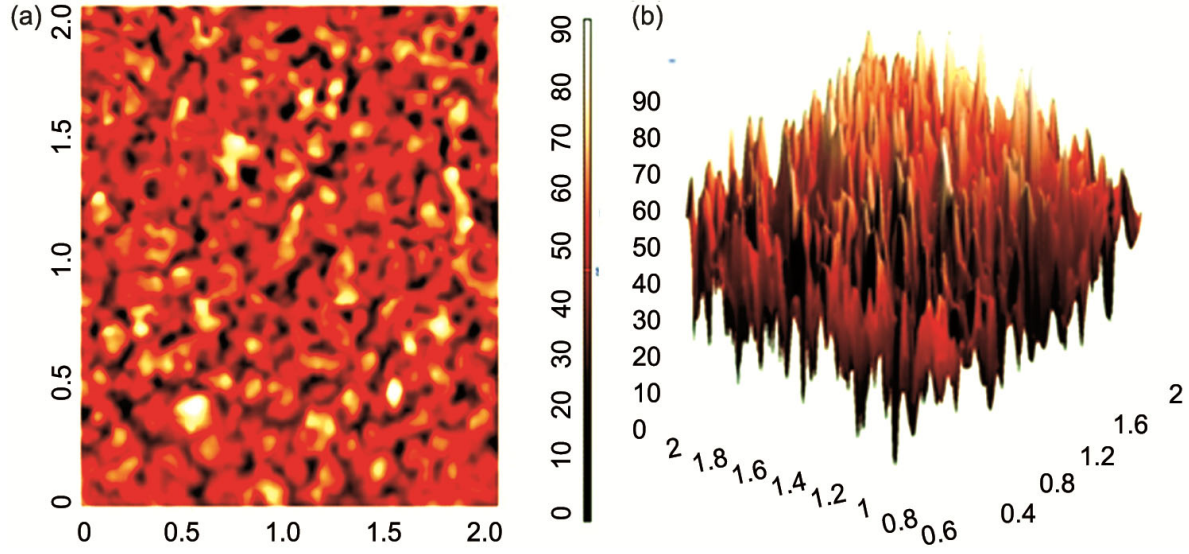

Fig. 4 — 2D and 3D AFM images of hydrogenated Pd/Mg thin films.

respectively. The surface roughnes is increased due to the deformation of surface atoms and volume expansion leading to increment in grain size after hydrogenation[19, 26, 29].

3.2 Hydrogen induced resistance response study

Hydrogenation and dehydrogenation of Pd/Mg films were carried out in a custom built hydrogenation unit[17]. Hydrogenation of Pd/Mg films was carried out at constant 2 bar hydrogen gas atmosphere at room temperature but dehydrogenation was carried out at various temperatures (RT, 50 °C and 100 °C). Electrical resistance variation has been tested in-situ during hydrogenation/dehydrogenation process using two probes by electrometer (Keithley) attachments with custom built hydrogenation unit[14, 17].

The relative change in resistance (R) = $(R_H - R_0)/R_0$, where R_H is the resistance of the film sample at a particular H_2 pressure and (R_0 = 3Ω) is the resistance of as-deposited Pd/Mg thin films.

Figure 5 shows the relative change in resistance (R)/sensing property of thin film samples for 2 bar H_2 and without hydrogen (low vacuum). During hydrogenation at room temperature, hydrogen gas is exposed to film sample and resistance of the film is found to be increased, This change in resistance may be due to two reasons: (i) the resistance change of the Pd capping layer, i. e., the Fermi level shift due to the increased filling of free charge careers (electrons) of the absorbed hydrogen, (ii) the resistance change of the Mg layer, i. e., transition from metal (Mg) to insulator (MgH_2). However, large percentage changes in resistance of the Pd/Mg layer is due to the formation of MgH_2[16, 19]. These two (hydrogenation of Pd and Mg) processes occur simultaneously.

The 2% resistance change is found within ~ 60 sec after hydrogen exposure and achieves its maximum of 37 % after 10 min duration. Dehydrogenation was carried out at various temperatures (RT- 100 °C) for more than 1hr in low vacuum (~ 10^{-3} Torr). From Fig. 5, it has been observed that the change in resistance is extremely low during dehydrogenation process at RT and 50 °C. This is due to the high binding energy (bond enthalpy) of MgH_2 and the given temperature (RT-50 °C) is not enough to break the bonding between hydrogen and Mg in MgH_2 system[30]. After dehydrogenation at 100 °C, resistance of the sample start to decrease fast. It is found that the removel of hydrogen from MgH_2 (dehydrogenation behaviour) is not similar to that of absorption of hydrogen in Mg (hydrogenation process). Firstly, the resistance drops rapidly then it decreases very slowly. The initial fast change is due to the change of the resistance of Pd capping layer and slow change is caused by the hydrogen desorption from MgH_2 layer[31]. Resistance of the film sample completely decreases after remove of all hydrogen and attain its origin value of as-deposited Pd/Mg films. The complete removal (desorption) of hydrogen takes about more than 1 h. This is because of the larger thickness (160 nm) of the Mg films in Pd/Mg system, cause higher desorption temperature or longer time[29].

3.3 Optical transmittance measurement

Figure 6 shows the transmittance spectra of as-deposited and hydrogenated Pd/Mg thin films on glass substrate. A significant change in optical transmittance

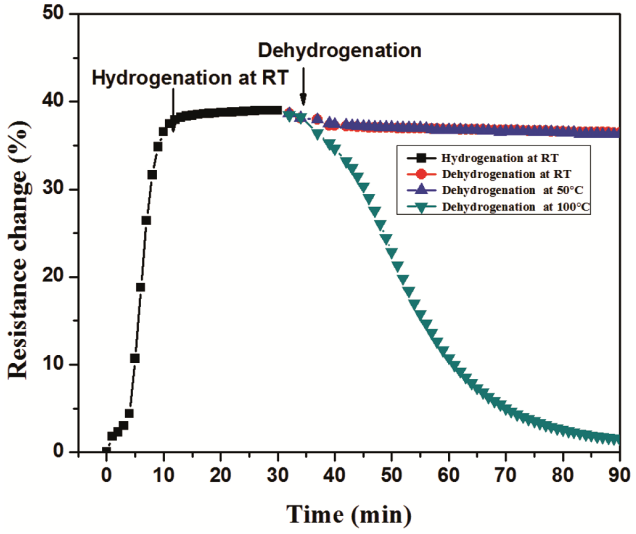

Fig. 5 — Resistance variation of Pd/Mg thin film during hydrogenation and dehydrogenation process.

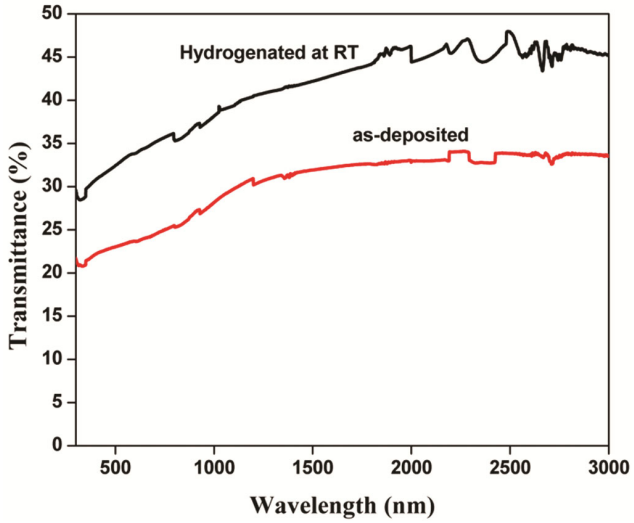

Fig. 6 — Transmittance spectra of as-deposited and hydrogenated Pd/Mg thin films.

has been observed after inclusion of hydrogen. It is evolved in the research as a 'switchable mirror' which can be switched from the mirror state (Mg, metallic film) to the transparent (MgH_2, hydride film) state upon hydrogen inclusion (hydrogenation)[32-34]. This is because of MgH_2 is theoretically a large band gap insulator[31]and transparent. Therefore, the optical transmittance of Pd/Mg film is changed. It has been found that, the transmittance is increased upon hydrogen absorption. Hence, transmittance change means that a considerable amount of MgH_2 is formed after hydrogenation at room temperature and it has been confirmed from results of XRD and electrical resistance studies.

4 Conclusions

Pd/Mg thin films have been deposited on glass substrate by pulsed laser deposition (PLD) technique. Pd-capped Mg film shows hydrogen absorption at room temperature and hydrogen desorption (dehydrogenation) at 100 °C. The studied Pd/Mg thin films are found very sensitive to hydrogen gas and its response time is ~ 60 s. These hydrogen sensing studies prove that Pd/Mg thin films can be used as low cost hydrogen sensing material. Although, some modifications are required to improve desorption temperature and time. A switching from mirror-like surface to transparent surface has been observed after H_2 inclusion in Pd/Mg thin films. The change in optical transmittance during hydrogenation reflects that Pd/Mg films can be used as low cost switchable mirror also.

Acknowledgement

All authors would like to thank Prof. Ramesh Chandra for providing, PLD, FE-SEM and XRD facilities at Institute Instrumentation center, IIT Roorkee, India. The financial assistance for this work by UGC, Govt. of India [No. F.30-303/2016 (BSR), F. D. Dy. No. 11299] is gratefully acknowledged.

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