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A room temperature hydrogen sensor based on Pd–Mg alloy and multilayers prepared by magnetron sputtering

Yogendra K. Gautam [a], Amit Sanger [b], Ashwani Kumar [b], Ramesh Chandra [b,*]

[a] Department of Physics, C. C. S. University, Meerut 250004, Uttar Pradesh, India
[b] Nanoscience Laboratory, Institute Instrumentation Centre, Indian Institute of Technology Roorkee, Roorkee 247667, India

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ABSTRACT

In the present study, we report the hydrogen sensing properties of sputter deposited tri-layers, multi-layers and alloy thin film of Pd and Mg materials. The change in electrical resistance is found to be reversible at room temperature during hydrogenation/dehydrogenation process for both the multi-layers and alloy thin film. The response time for Pd/Mg/Pd tri-layers, Pd/Mg/Pd/Mg/Pd multi-layers and Pd/Mg–Pd alloy is 4.5, 3.5 and 3 s, respectively. The hydrogen desorption from Pd/Mg/Pd/Mg/Pd multi-layers is enhanced by "cooperative effect" caused by elastic interaction within interfacial region of Pd and Mg films. While, the room temperature desorption with fast kinetics for Pd-capped Mg–Pd alloy thin film is due to reduction in binding energy. The study suggests that these Pd–Mg based alloy thin film and multilayers have the potential to be used as room temperature H_2 gas sensor.

Introduction

Hydrogen is a promising potential fuel for vehicles to overcome the problems related to fossil fuel and climates. It can also be converted into electricity by fuel cells [1,2]. It is also used in medicine, space exploration, production of industrial chemicals and food products [3]. Hydrogen forms an explosive mixture with air once its concentration exceeds beyond the explosion limit (4%). Hence, safety is an important issue while considering hydrogen as a fuel for the future. As hydrogen can't be detected by human senses, a highly sensitive and selective sensor is today's necessity. The research on detection and concentration measurement of hydrogen is going on since early eighties [4]. However, there is a need of faster, accurate and selective detection of hydrogen gas in various areas of industry for monitoring and controlling hydrogen concentration. Many materials that respond to H_2 gas have been studied for its sensing behaviour. Mostly hydrogen sensors use semiconductor materials such as ZnO nanorods and thin films, SnO_2 coated carbon, WO_3 and NiO thin films [5–10]. Due to high operation temperature (≥200 °C), metal oxide-semiconductor based sensors consume relatively large

* Corresponding author. Tel.: +91 1332 285743; fax: +91 1332 286303.
E-mail address: ramesfic@iitr.ac.in (R. Chandra).
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power for device operation and there is a possibility of explosion in case of hydrogen leak. Some notable materials like, Pt nanoparticles, graphene based materials and tungsten nanowires have also been analysed for their hydrogen sensing properties [11–15]. None of these sensing device full fill the hydrogen economy demand in terms of work efficiency, reliability, response time and cost. However, the detection and monitoring the hydrogen gas in terms of requirement criteria, has a great deal of importance. Pd-based nanomaterials are very selective to hydrogen due to low activation barrier to adsorption, high hydrogen solubility and favourable reaction kinetics. Change in electrical resistance of Pd thin film after hydrogen exposure, proposed Pd as a hydrogen sensing material [16,17]. The literature available on Pd films reported a considerable good response time (~10–120 s) for low hydrogen concentration (~4%). While, response time has been found to be increases (>120 s) at higher hydrogen concentration. The Pd film was also found mechanically unstable (peeled off) at higher hydrogen concentration [18–23].

Mg is considered as one of the most promising hydrogen storage materials due to its high storage capacity, light weight and low cost [24,25]. In addition, the optical and electrical properties of Mg-based thin films changes upon hydrogen absorption and desorption process [26,27]. As a result, Mg-based thin films could potentially be applied as hydrogen sensors, solar absorbers and switchable mirrors [28–30]. Recently, lot of research work has been done by various groups in development of hydrogen gas sensors. Sputtered deposited Pd (40 nm)-capped Mg (10 nm) thin film based device showed the optical change (reflection to transmission) due to metal to metal hydride transition. This optical sensor was read out continuously in hydrogen partial pressure of 200–4000 Pa. The 80% of the response is realized within 500 s at about 0.04 bar hydrogen concentration [31]. $Mg_{70}Ti_{30}$(50 nm) thin film capped with a 30 nm P catalytic layer was found capable of detecting hydrogen at pressures down to 10% of the lower flammability limit in a timescale of seconds [32]. Yoshimura et al. reported the hydrogen sensing property of sputtered deposited Pd/$Mg_{0.9}Pd_{0.1}$ thin film of thicknesses 10 nm of Pd and 40 nm of Mg–Pd. The alloy films showed a good hydrogen sensing property (response time 10 s) at room temperature by monitoring its resistance change at low concentration of H_2 (4% of H_2 in Ar gas) [33]. Hydrogen sensing properties of Pd-capped magnesium–nickel alloy thin films were analysed by monitoring the resistance or transmittance change of the film. All reported studies reveal the dependence of response time on hydrogen concentration range. The hydrogen sensor using Pd/Mg–Ni thin film showed wide sensing range (10 ppm–10%) with response time of (5–100 s) [34].

In previous study, we have reported the hydrogen sensing properties of PLD deposited Pd-capped magnesium thin films. In which hydrogen was loaded at room temperature while desorption was at 100 °C i.e. film didn't show reversible (loading/deloading) characteristics at room temperature. The response time of Pd-capped magnesium thin films was 60 s at 2 bar hydrogen concentration [35]. Recent studies report the role of catalytic effect on hydrogenation/dehydrogenation properties of magnesium hydride [36–40]. These reports concluded the role of small desorption pathways for better hydrogen desorption [41,42].

In the present investigation, we report the hydrogen sensing property of tri-layers, multilayers and alloy thin film of Pd and Mg materials. We carried out the structural, morphological and electrical studies on alloy thin film and multilayers after hydrogenation/dehydrogenation process. The present investigation gives desirable sensing properties of alloy thin film and multilayers of Pd and Mg materials. A complete and reversible hydrogenation-dehydrogenation for Pd–Mg alloy thin films has been achieved at room temperature. Therefore, Mg and Pd based alloy thin films can be used as a room temperature hydrogen sensor with good reversibility, fast response and stability.

Experimental details

Thin films of (Pd/Mg/Pd, Pd/Mg/Pd/Mg/Pd and Pd/MgPd) were deposited on p-Si (100) substrate using Mg (99.98% purity) and Pd (99.95% purity) targets (2" diameter and 5-mm thick) by DC magnetron sputtering. For Pd/MgPd formation, co-sputtering of Mg and Pd targets was carried out for alloy thin film on Si (100) substrate, and then a thin Pd layer was subsequently deposited onto the alloy film for the enhancement of hydrogen uptake kinetics. The sputtering chamber was initially evacuated to high vacuum (~3×10^{-6} Torr) by turbo molecular pump. Thereafter, high purity (99.99%) inert gas (Ar) was used in sputtering. The targets were pre-sputtered for 5 min. The sputtering parameters for all samples are shown in Table 1.

Sample characterizations

XRD measurements were carried out using CuK_α radiation in X-ray diffractometer (Bruker D8 Advanced) with $(\theta - 2\theta)$ geometry for structural analyses. Field emission scanning electron microscope (FEI, Quanta 200F) was used to characterize the cross sectional view of as-deposited samples. Atomic force microscopy (NT-MDT, Ntegra), was used in semi contact (tapping) operating mode to analyse the surface morphology of the as-deposited and hydrogenated samples. The change in electrical resistance during hydrogen loading/deloading was analysed in-situ by using a current source meter (Keithley 6221) and nano voltmeter (Keithley 2182A) with two probes as reported earlier [43]. Hydrogen loading for all samples was carried out at room temperature in 2 bar H_2 (99.99% purity) atmosphere. Hydrogen deloading was performed at various temperatures (RT-100 °C) in low vacuum.

Results and discussion

Film structure and morphology

Fig. 1 shows XRD patterns of as-deposited, hydrogen loaded and deloaded Pd/Mg/Pd tri-layers, Pd/Mg/Pd/Mg/Pd multilayers and Pd/MgPd alloy thin films. The as-deposited tri-layers show XRD peaks corresponding to a hexagonal-Mg (002) plane at 34.67° (JCPDS-ICDD no. 040770) and face centred cubic-Pd (111) plane at 40.09° (JCPDS-ICDD no. 11141). After hydrogenation (2 bar H_2, 35 °C), along with Pd, three different phases of α-MgH_2(JCPDS-ICDD no. 120697) at 27.87°, 37.98° and