

Structural, Electrical and Optical Properties of Mg-Ni Thin Films for Hydrogen Storage Applications

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Abstract

Using the magnetron sputtering technique, Mg-Ni (150nm) bilayer thin films were deposited onto the simple, and ITO coated glass substrates. To obtain proper mixing and inter diffusion of thin film structure, annealing of the prepared thin films was made at constant temperature 523 K. The surface morphology of thin films confirms the uniform deposition of the Mg-Ni thin films on substrates. The Raman spectroscopy of thin films shows that the intensity of Raman peaks is decreased as the hydrogen pressure increases and variation in the intensity peak confirms the existence of hydrogen in the prepared film. The d.c. conductivity of thin films were observed at different hydrogen pressure (10 - 40 psi) for both the as-deposited and annealed thin films and the variation in the conductivity after hydrogenation was found out. In Uv-Vis spectroscopy, it was found that the optical bandgap of thin films increases with the increase of hydrogen pressure. The deviations in the structural, electrical and optical properties after hydrogenation indicate that Mg-Ni thin films may be used for solid state hydrogen storage applications.

Keywords: Thin film, Hydrogenation, Surface morphology, Raman spectroscopy, Conductivity, Optical energy bandgap

Introduction

Hydrogen (H₂) has been considered sustainable and clean energy for the future. It is also more environmentally friendly than other carbon-based fuels [1]. The hydrogen storage materials are used in practical applications with excellent hydrogen storage capability. The age-old technologies are used for hydrogen storage purpose after modification in their physical state like gaseous/or liquid forms, still they have several practical problems resulting from its low boiling point and density [2]. Currently several researchers are being focused on the solid-state hydrogen storage in their research and are suggesting the possibilities of hydrogen storage in metallic hydride phases. The solid storage of hydrogen is the safest alternate system in the present. The solid hydrogen storage has comparatively high hydrogen storage capacity than pressurized gas and cryogenic liquid forms [3,4]. In solid state hydrogen storage, the use of thin films structure has become very significant as absorption and desorption process of hydrogen takes place at the surface of the material. The fast charging and discharging rate of thin film hydrides structure over the bulk hydrides are the main benefits of thin film to use for hydrogen storage purpose. Magnesium (Mg) has been broadly examined as a potential hydrogen storage material and it comprises some required characteristics vital for its validity. Mg is the suitable element for solid hydrogen storage due to being light-weight, naturally abundant and low-cost. Mg-hydride, MgH₂, is mainly attractive because of its very high reversible hydrogen capacity (7.6 wt%) [5]. The alloying of Mg with the transition metals can result in improved dissociation mostly due to the presence of d-electrons [6]. A very attractive progress in the metal hydrides was observed during the discovery of magnificent changes in the optical and electrical properties of Y and La thin film hydrides near their metal insulator transition [7-9]. Among the various Mg-based hydrogen storage alloys, Mg-Ni hydrogen storage alloys are the most studied, which have comparatively higher hydrogen storage capacity and have better hydrogen absorption/desorption activity. Though, Ni is a special case with a high catalytic effect in spite of its electro-negativity. It has been believed that the formation of the Mg-Ni compound might play a significant role in improving the hydriding kinetics of the Mg-Ni system [10-14]. The Mg-Ni-H system has been investigated since many years, typically because of the large hydrogen storage capacity 3.6 wt% as Mg₂NiH₄ [15]. The dazzling optical changes upon absorption of hydrogen have been observed in yttrium and lanthanum, the thin film

is changed from metal to insulator transition on exposure to hydrogen. The same property also own Mg alloyed rare earth metal hydrides [16]. Hence, a range of attempts have been brought forth to study the Mg thin film for the use of solid-state hydrogen storage purpose [17-20]. The drastic changes in optical appearance of Mg_yTM_x (TM=Ni, Co, Fe) thin films have been observed upon the hydrogen is exposed at room temperature and the alloys made of Mg and transition metals such as Ni, Co, Fe and Mn are switched reversibly [21,22]. Among the various metal hydrides, Mg_2NiH_4 has been acknowledged as a favorable alloy for having fine hydrogen storage capacity along with an enhanced kinetics compared to the MgH_2 [23]. In the present study the surface morphology, Raman spectroscopy, I-V characteristics and UV-Vis spectroscopy of Mg-Ni thin film have been studied for hydrogen storage applications.

Materials and methods

The advantage of the magnetron sputtering is that it provides the controlled fabrication of good quality coatings with very good adhesion to substrate. The metallic targets of Mg (99.99 %) and Ni (99.99%) were used to prepare bilayer Mg-Ni (Mg-100nm and Ni-50nm) thin films by using magnetron sputtering technique. The deposition rates of Mg and Ni film were 0.40 and 0.42 Å/s, respectively when the thin films were deposited. During the deposition of thin film base vacuum and working vacuum in magnetron sputtering were 10^{-7} mbar and 10^{-3} mbar, respectively. The substrates were pre-cleaned then placed into the coating chamber and before unloading the samples from sputtering unit. Annealing of the samples was done at temperature 523K for mixing of the Mg-Ni thin films and to get homogeneous structure. Hydrogenation of the samples was made at 10-40 psi hydrogen pressures, for this the samples were kept in hydrogenation cell, where hydrogen gas was present at different pressures for an hour. To study the surface morphology of annealed Mg-Ni film, the SEM analysis was carried out using Nova Nano Field Emission Scanning Electron Microscope (FE-SEM). Raman spectroscopy of both annealed and annealed hydrogenated thin films were done by using the R-3000 Raman system with continuous wave green laser at a constant wavelength 532 nm. I-V spectra of the samples were obtained using the Keithley-2,400 high current source measuring unit at room temperature. The range of applied voltage was -5.0 to +5.0 volts along with increasing step 0.1 volt. The UV-1800 Shimadzu spectrophotometer was used to get UV-Vis absorption, the absorption data was recorded in the visible range of wavelength (300-800 nm). All characteristics of the prepared samples were taken at room temperature.

Results and discussion

Surface morphology of annealed Mg-Ni thin films is shown in **Figure 1**. The surface morphology of film indicates the uniformly deposition of Mg-Ni thin film. The surface morphology of the annealed samples was recorded using the FE-SEM. The contrast in FE-SEM image suggests that the prepared Mg-Ni film was uniformly deposited onto the substrate using a sputtering technique with fine adhesion. Raman spectra of the Mg-Ni thin film are shown in **Figure 2**. The Raman spectroscopy is used to find the structural defects as well as impurities in the film structure. In Raman spectra of the films one strong peak was observed at 110 cm^{-1} and intensity was decreased after hydrogenation. It was also observed that the peak was shifted towards the left side after hydrogenation of film at 20 and 40 psi H_2 pressure. The decrement in intensity of Raman peaks recommends the phase change due to hydrogenation and hydrogen builds the bonding with metal interstitial. This validates the existence of hydrogen in the Mg-Ni thin films. In previous years, many researchers have also investigated the existence of hydrogen in thin film materials by using Raman spectroscopy [24,25]. The electrical property of Mg-Ni thin film like I-V characterizations provides the information regarding the electronic effects of hydrogen on film structure. It was seen in the I-V characteristics that as-prepared thin film represents the ohmic behavior for both the positive and negative ranges of voltage due to the free flow of Ni electrons across the junction, whereas annealed thin film shows the partially semiconducting nature due to the proper mixing of thin film after annealing.

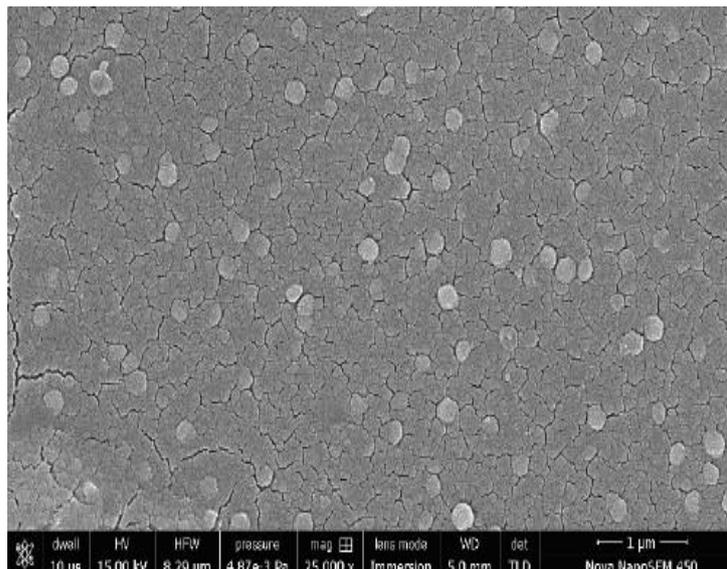


Figure 1 Surface morphology of annealed Mg-Ni thin films.

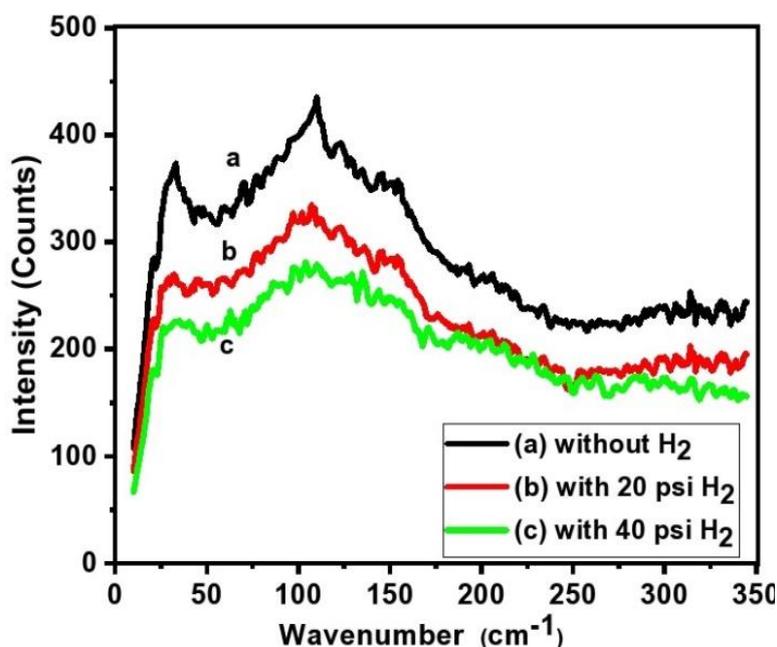


Figure 2 Raman spectra of annealed hydrogenated Mg-Ni thin films.

Figure 3 shows the I-V characteristics of as-prepared Mg-Ni thin films. It was observed that I-V curve of as-prepared thin films shows partially straight line and d.c. conductivity increases with the increase of the hydrogen pressure. It can be explained that hydrogen behaves like a donor element and reveals the charge shift from hydrogen to the film structure. As result a conducting bridge is formed between the defects spots available in the film. Thus, decrease in the resistance occurs with increasing pressures of hydrogen and an increase in d.c. conductivity was found as the pressure of hydrogen increased. **Figure 4** shows the current-voltage spectra of annealed hydrogenated Mg-Ni thin films. It was found in the I-V curve that the annealed thin film shows the partially semiconductor behavior and the d.c. conductivity of the thin films decreases with increasing the pressure of hydrogen (10-40 psi). The d.c. conductivity for annealed thin film was found to be decreased from $6.28 \times 10^6 \Omega^{-1} \text{m}^{-1}$ to $9.36 \times 10^5 \Omega^{-1} \text{m}^{-1}$. The decrease in the conductivity suggests that hydrogen passivated the defects at the interface of film.

Also, during the hydrogenation process, hydrogen gets electrons from the conduction band and blocks the flow of charge carriers across the interface [26].

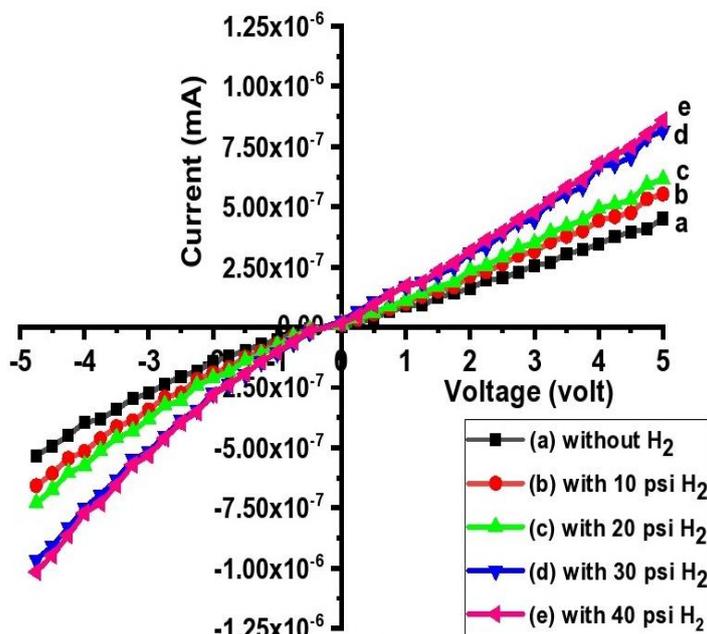


Figure 3 I-V characteristics of as-prepared hydrogenated Mg-Ni thin films.

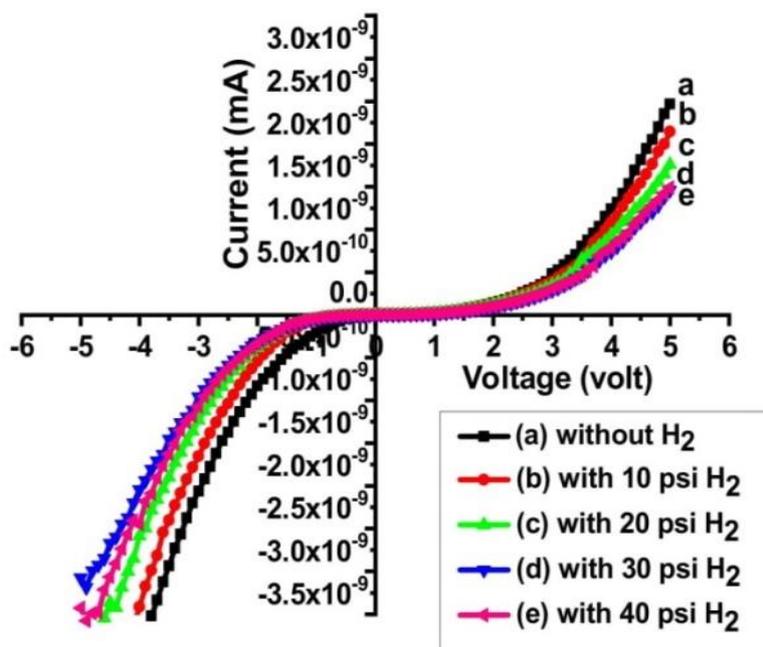


Figure 4 I-V characteristics of annealed hydrogenated Mg-Ni thin films.

The electronic properties of materials are strongly affected by hydrogen and hydrogen can also persuade electrically active defects. Observation of electrical properties gives evidence about hydrogen's electronic defects on materials [27,28]. The similar results have been reported in our previous work and the conductivity of thin film were decreased with increase hydrogen pressure during hydrogenation process [29,30]. The polycrystalline thin film of CdTe has been investigated after being exposed to

hydrogen gas and found the d. c. conductivity decreases as hydrogen pressure increases. The decrement in the conductivity of thin films may suggest that the reduction of free charge carriers during the hydrogenation of the thin film [31,32].

Figure 5 shows the variation in absorption of thin films. It was observed from the spectra that absorption of the film increases after hydrogenation of the film. The absorption of film material and its hydrides states may be understood by assuming the good intermixing of Mg and Ni at the interface of the film. The variation in absorption after hydrogenation can be explained as the introduction of Ni layer along with Mg hydrides endorses the formation of complex hydride phase, which is accountable for the presence of hydrogen and increases hydrogen content in the film structure [33]. **Figure 6** shows the energy bandgap spectra of the bilayer Mg-Ni thin films. To calculate the optical forbidden energy bandgap of thin film structures Tauc relation was used [34].

$$\alpha h\nu = A(E_g - h\nu)^{1/2}$$

where E_g - optical energy bandgap, α -absorption coefficient, $h\nu$ - photon energy and A- a constant. The direct bandgap of the films were calculated by $(\alpha h\nu)^2$ vs $h\nu$ spectra plotted for the samples, with the linear vicinity extrapolation to lower energy. It was observed from the spectra that the optical energy bandgap increases as hydrogen pressure increases. It may be due to phase transformation of the film after hydrogenation and the diversity in optical energy bandgap with hydrogen pressure also indicates the phase change of film from metal to semiconductor [35,36]. It have been reported that the Mg-Ti [37-39], Mg-Fe [37,40], Mg-Co[41] and Mg alloy films[42,43] improve the hydrogen storage capacity by varying the degrees in respect to pure Mg and bulk materials films. In the complex metal hydrides, the optical bandgap for Mg_2NiH_4 , Mg_2CoH_5 , and Mg_3MnH_7 have been observed as 1.6, 1.9 and 2.56 eV, respectively [44,45]. These studies have suggested that metal hydride shows phase transformation in hydride formation. It has also been reported in the theoretical studies that MgH_2 goes under the number of phase transitions with hydrogenation [46,47].

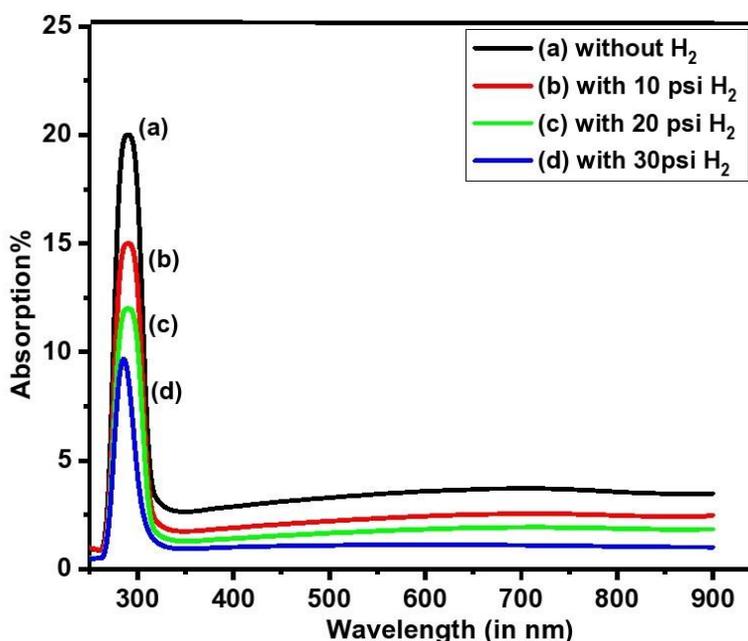


Figure 5 Optical absorption spectra of Mg-Ni thin films.

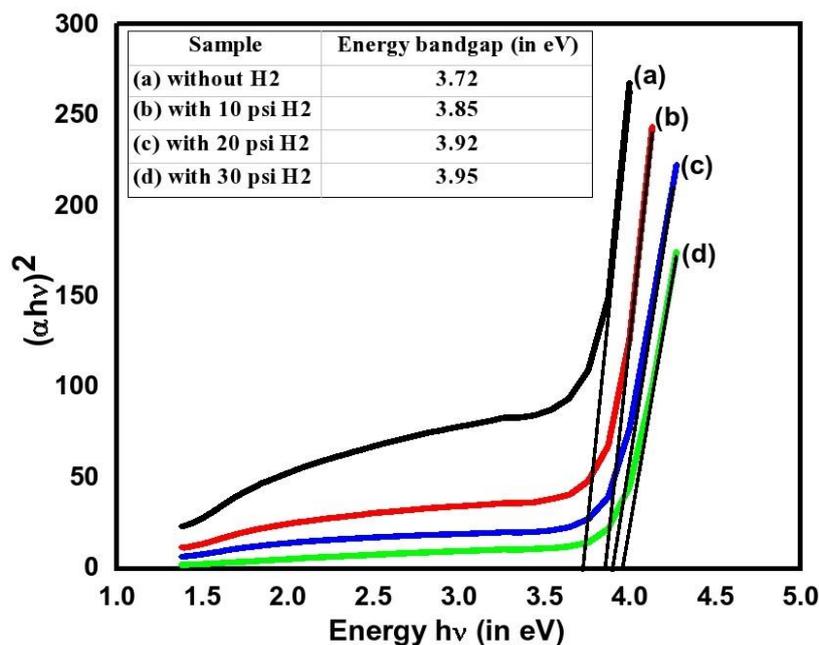


Figure 6 Optical energy bandgap spectra of Mg-Ni thin films.

Conclusions

In the current study, the effect of hydrogenation on optical, electrical and structural properties of Mg-Ni thin films has been investigated. In the study, it was found that hydrogen gas tailored the electrical and structural properties. The surface morphology validates the uniform deposition and proper mixing of prepared Mg-Ni thin film structure. In the Raman spectroscopy, decrease in intensity of peaks suggests that a bonding is built between the hydrogen and metal interstitial and confirms the presence of hydrogen in Mg-Ni thin films. It is concluded from the above study that as-deposited Mg-Ni thin films show ohmic behavior and d.c. conductivity is increased with the increasing hydrogen pressure as hydrogen behaves like a donor element in the films. After annealing the prepared Mg-Ni thin film shows the partially semiconductor nature and conductivity decreases as hydrogen pressure increases. The decrease in the conductivity suggests that hydrogen passivates the defects at the interface of film. Also, during the hydrogenation process, hydrogen gets electrons from the conduction band and blocks the flow of charge carriers across the interface. The change in the optical energy gap with hydrogen pressure indicates the phase change of the film from metal to semiconductor. All investigations are indicating the Mg-Ni film may be used as solid-state hydrogen storage.

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