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Research Article

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Hydrogen Storage Characteristics of Mg-based Mn Thin Films

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ABSTRACT

This article reports the hydrogen storage characteristics of Mg-Based Mn thin film. The Mg-Mn thin films prepared using thermal evaporation method at pressure 10-5torr. The deposited films were annealed in vacuum at constant temperature 500K for one hour to get a homogeneous structure. Annealed thin films have been separately hydrogenated at different hydrogen pressure (20-60 psi) for 30 min. these films have been characterized and Optical band gap has been found to be increase with hydrogenation; it may be due to hydrogen accumulation at interface. Pristine film shows ohmic behavior and after annealing it shows semiconductor nature and also the conductivity of thin films has been found to be decreased due to hydrogenation because hydrogen takes electron from conduction band of metal as anionic model. Concluded the enhanced hydrogen affinity at the film substrate interface and suggested the study of complex hydride formation in thin films might give valuable information for the use of these Mg-Mn structures for hydrogen storage as well as solar collector materials.

Key words: Thin film, annealing, hydrogenation, optical and electrical properties

INTRODUCTION

A group of Mg-based hydrides stand as promising candidate for competitive hydrogen storage with reversible hydrogen capacity up to 7.6 wt% for on-board applications [1]. The three different families of metals and alloys have been identified to exhibit switchable properties from metallic to transparent during hydrogenation: (i) rare earth hydrides RE–H,[2] (ii) RE–Mg–H, [3] and (iii) Mg–TM–H (TM =transition metal such as Fe, Co, and Ni) [4,5]. Most of them have a band gap whose energy corresponds to the range of visible radiation. Richardson et al.[6,7], discover that Mg based films absorb hydrogen very easily, while in bulk samples hydrogenation requires high temperatures (500 to 600K) and pressures of 105 to 106 Pa , for thin films it occurs readily at room temperature at low pressures, and it opened the way to the third-generation switchable mirrors. Mixed metal thin films containing magnesium and a first-row transition element exhibit very large changes in optical and electrical properties on exposure to hydrogen gas [8, 2]. Similar behavior was subsequently found in Mg-rare-earth films and magnesium transition-metal alloys, such as Mg_2CoH_5 [9], $Mg_6Co_2H_{11}$ [10] and Mg_2FeH_6 [11], the band structure calculations which support experimental evidence for semiconductor behavior in these materials [9, 11]. The various scientists observed variation in optical band gap of complex hydrides and found 1.6 eV in case of Mg_2NiH_4 [12], 1.9 eV in case of Mg_2CoH_5 [13] and 2.56 eV for Mg_3MnH_7 [14]. The optical properties of Mg-TM (Ni,Co,Fe,Mn) also carried out by Lohstroh et.al.[15] and they suggested that the nucleation of hydrides start at the film substrate interface and remarkable optical black state of intermediate hydrogen concentration. Hydrogen is omnipresent and easily incorporated in materials. Interstitial hydrogen is a fast diffuser. It can bind to native defects or to other impurities, often eliminating their electrical activity-a phenomenon known as passivation [18]. Electrical measurements such as current/voltage, capacitance/voltage and hall measurements, provides detailed information about the electric effects of hydrogen [16-17]. The conductivity of semiconducting thin film has been found to be decreased with hydrogenation [16, 17]. The interaction of hydrogen in a metal hydride can be understood by using the anionic model [18]. The effect of hydrogen pressure on FeTi and FeTi–Mn observed by Singh et al. [19] and suggested that hydrogen takes electron from inter-metallic structure. The increase in resistivity ratio with increasing hydrogen absorption time means that hydrogen takes more electrons from the conduction band of the intermetallic compound and accelerates the hydrogen absorption capacity of samples [20, 21]. The second generation switchable mirrors exhibit an absorbing, black state at intermediate hydrogen concentrations, due to the coexistence of nano-crystalline reflecting and transparent phases [5, 22]. The magnesium based hydrides can be used in several applications such as switchable mirrors as indicator layers [20], smart windows [23], switchable absorbers [26] and fiber optic hydrogen sensors [24].

In the present work, we are reporting the preparation of Mg-Mn thin films by thermal evaporation technique and its characterization through UV–vis spectrophotometer and current–voltage measurements of pristine as well as annealed hydrogenated thin films. The purpose of this work is to evaluate the role of annealing temperature and hydrogen and suggested that Mg-Mn thin films structures can be used for hydrogen storage as well as solar collector.

EXPERIMENTAL TECNNIQUE

Sample Preparation

Thin films of Mg-Mn have been deposited layer-by-layer onto a simple glass as well as indium-tin-oxide (ITO) substrate by thermal evaporation technique (Hind High Vacuum) under vacuum of 10-5torr. Mg granules (99.99%) & Mn powder (99.99%) pure were used for the present study and these kept into two different boats of tungsten material in the vacuum chamber. The source to substrate distance was kept 15cm in each case. To get good adhesion we have used substrate heater having constant temperature of 80-90oC. Deposition of Mg-Mn thin films has been performed by stacked layer method. The thickness of Mg-Mn thin films was 400nm measured by quartz crystal thickness monitor (Hind Hi Vac Thickness Monitor Model DTM-101).

Annealing

To get homogeneous structure and interdiffusion of Mg and Mn layers, vacuum thermal annealing of thin films have been performed in a vacuum of 10–5 torr by using vacuum coating unit, where samples were kept on a heater at constant temperature 500K for one hour. The temperature of heater was measured by using CIE-305 thermometer.

Hydrogenation

The vacuum annealed Mg-Mn thin films have been hydrogenated by keeping these in hydrogenation cell, where hydrogen gas was introduced at different pressures (20-60 psi) for 30 minutes and obtain annealed hydrogenated samples.

Optical Characteristics

The optical transmission spectra of vacuum annealed and annealed hydrogenated thin films are carried out in the wavelength range 300–800nm with the help of Hitachi Spectrophotometer Model-U3300.

Electrical Characteristics

Transverse I-V characteristics of thin films have been observed by Keithley-238 high current source measuring unit. The applied voltage was in the range of -2.0 to +2.0 volts with increasing step of 0.1 volt. For I-V characteristics, electrode contacts have been made using silver (Ag) paste on the thin films. I-V characteristics of thin films have been monitored with the help of SMU Sweep computer software.

RESULTS AND DISCUSSION

Optical Characteristics

Optical transmission spectra of Mg-Mn thin films deposited onto a glass substrate were studied at room temperature in the range of wavelengths 300 - 800nm. Optical transmission spectra of as-grown, vacuum annealed and annealed hydrogenated thin films are shown in Fig. 1 It may be attributed that transmission of annealed thin films is higher than the as-grown thin films, indicating the mixing of thin films due to the annealing. After annealing there is an increase in crystallinity or grain growth, as confirmed by structural characteristics. Annealed hydrogenated thin films show higher transmission comparative to as-grown and annealed thin films and increases with increasing hydrogenation pressure. Therefore, it may be attributed that hydrogen has passivated defects at the surface or interface of thin films resulting in an increase in transmission through hydrogenated thin films.

The nature of the transition can be investigated on the basis of the dependence of the absorption coefficient with the incident photon energy hν. For direct and indirect allowed transitions, the theory of fundamental absorption leads to the following photon energy dependence near the absorption edge: $\alpha h\nu = A(Eg-h\nu)m$ where hν and Eg are the photon and the band gap energy, respectively. In this relation, the values of m are 0.5 and 2 for direct allowed and indirect allowed transitions, respectively. The above relation is known as the Tauc relation [25]. So in the present work, we have used m = 0.5 and the intercept of straight line to energy axis $(\alpha h\nu)2 = 0$ used to find out the optical band gap. The plot of $(\alpha h\nu)2$ vs hν as-grown, vacuum annealed and annealed hydrogenated Mg-Mn thin films is shown in Fig. 2. This graph shows the value of optical band gap for films. The optical band gap of vacuum annealed thin film was found to increase from 3.21 to 3.20 eV due to variation of concentration and increasing the grain size of films with temperature [26] and increased from 3.35 to 3.50 eV in hydrogenated thin films with increasing pressure (20 to 60 psi) of hydrogen as shown in Fig. 3. The optical band gaps nearly agree with the reported band gap (2.56 eV) by E. Orgaz et al [14].

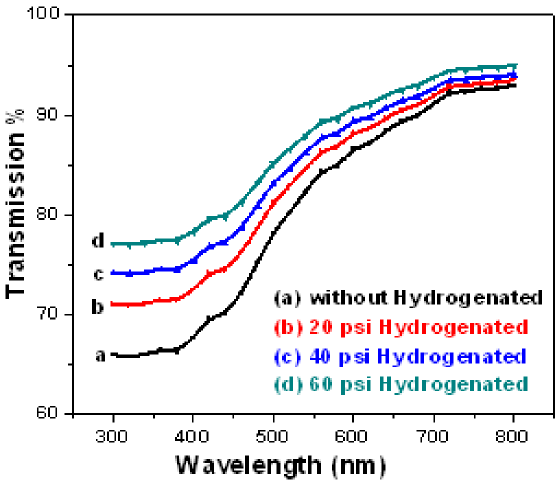

Fig. 1 Optical transmission spectra of vacuum annealed Mg-Mn at different hydrogen pressure

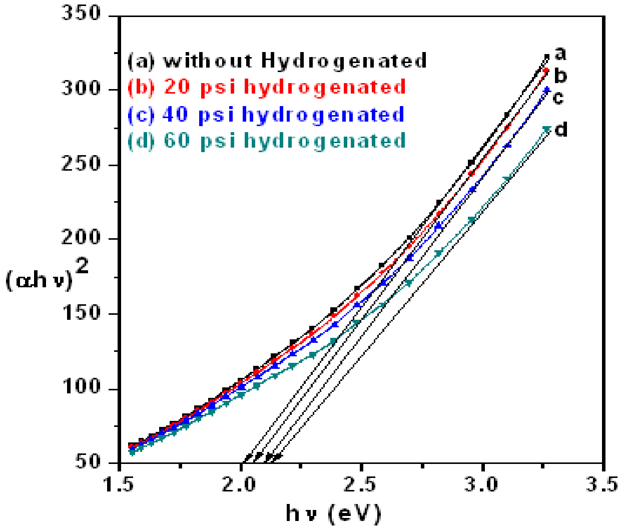

Fig. 2 Optical band gap spectra of vacuum annealed Mg-Mn at different hydrogen pressure

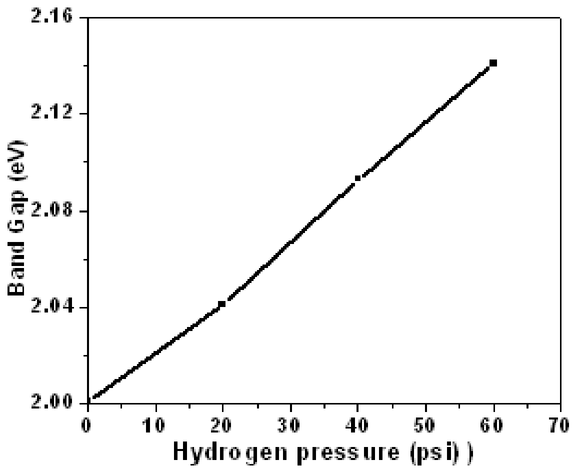

Fig. 3 Variation in optical band gap with hydrogen pressure of vacuum annealed Mg-Mn thin films

I-V Characteristics

Fig. 4 shows I-V characteristics curves for (a) as-grown and (b) vacuum annealed Mg-Mn thin film, in which (a) shows the partially straight line for both positive and negative ranges of voltage, indicating the ohmic behavior of the junction due to the free flow of Mn electrons across the junction, whereas (b) shows the partially semiconducting nature of the junction due to the annealing effect which causes the mixing or inter diffusion of thin film.

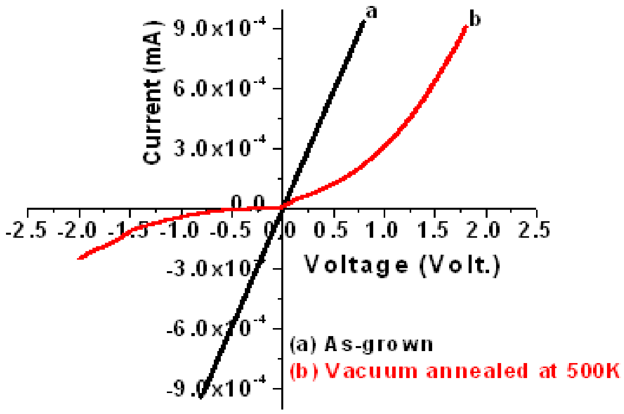

Fig. 4 I-V characteristics of (a) as-grown and (b) vacuum annealed Mg-Mn thin films

Fig. 5 shows that I-V characteristics of vacuum annealed hydrogenated Mg-Mn thin films and it have been found to be partially semiconducting nature and conductivity decreases with increasing pressure of hydrogenation due to the hydrogen interaction with semiconductor. It means hydrogen takes electrons from the conduction bands of Mn due to hydrogenation and blocks the flow of charge carriers across the interface and current decreases in forward as well as reverse direction. Hydrogen interacts with semiconductor and takes electrons from conduction band as anionic model [18].

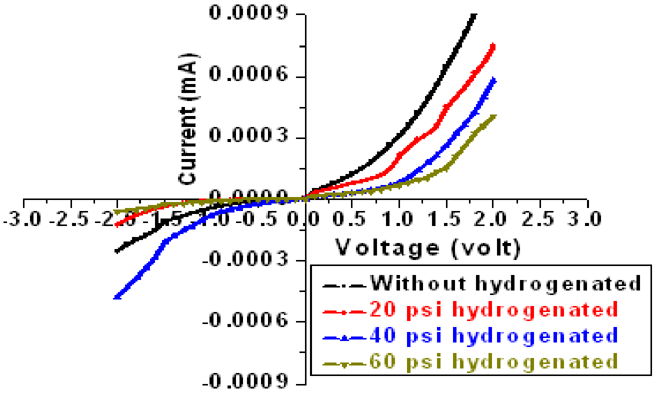

Fig. 5 I-V characteristics of vacuum annealed Mg-Mn at different hydrogen pressure

Table 1- Optical Band Gap and Conductivity of Mg-Mn Thin Film

H_2 pressure (psi)	Band Gap (eV)	Conductivity ($10^{-5}\ \Omega^{-1}$-m^{-1})
Without H_2	2.0108	7.6631
20 psi	2.0408	6.1253
40 psi	2.0932	4.8320
60 psi	2.1420	3.4212

CONCLUSION

From the above detailed study, we conclude that vacuum annealing may be used for mixing the thin film structure, because our optical band gap data as well as I–V characteristics show formation of Mg-Mn compound semiconductor. The hydrogenation and vacuum thermal annealing tailored optical and electrical properties of Mg-Mn thin films. Optical band gap has been found to be increase with hydrogenation; it may be due to hydrogen accumulation at interface. The conductivity has been found to be decreased due to hydrogenation because hydrogen takes electron from conduction band of metal as anionic model. Concluded the enhanced hydrogen affinity at the film substrate interface and suggested the study of complex hydride formation in thin films might give valuable information for the use of these Mg-based Mn thin film structures for hydrogen storage as well as solar collector materials.

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