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# EFFECT OF HYDROGENATION ON RAMAN SPECTRA, STRUCTURAL AND OPTICAL PROPERTIES OF Mg/Al THIN FILMS

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## ABSTRACT

The bilayer thin films of Mg/Al (400nm) were prepared in a vacuum system at pressure $10^{-5}$ torr. Structural, optical properties and Raman spectra of Mg/Al thin films are investigated before and after exposure to hydrogen. Hydrogenation of annealed thin films has been performed by keeping these in hydrogenation cell at different hydrogen pressures for 30 minutes. The UV–Vis absorption spectra of thin films have been carried out at room temperature in the wavelength range of 300–900 nm. The optical band gap was found to be increase with hydrogen pressure.

We have observed decrease and increase intensity of peaks in Raman spectra with hydrogen pressure. Increase in intensity of Raman peak may be due to phase transformation or formation of complex hydrides. The enhanced hydrogen affinity and formation of complex hydrides in thin films might give valuable information for the use of these bilayer thin film structures for hydrogen storage purposes. We have correlate decrease in peaks with molecular hydrogen absorption at interface of film and sharp intense due to covalently bonded hydrogen in Mg/Al bilayer film. The XRD confirm the hexagonal structure of thin films with increasing concentration of hydrogen.

**KEYWORDS:** Bilayer Thin Films, Xrd, Optical, Electrical, Structural Properties and Raman Spectra

## INTRODUCTION

The availability of a safe and effective way to store hydrogen reversibly is one of the major issues for its large scale use as an energy carrier. In order to develop suitable hydrogen storage materials, a detailed knowledge of the atomistic mechanisms of hydrogen motion in these systems is required. It becomes clear that in the new generation of advanced materials a proper engineering of alloy composition, surface properties, microstructure, grain size etc. is needed to design and control properties of materials, according to the requirement of the particular application. For this purpose, the ideal hydrogen storage material should have the following properties: high gravimetric and volumetric hydrogen density, fast kinetics of (de)hydrogenation near ambient temperature, long term stability and good thermal conductivity for removing the reaction heat.

Metal hydrides are a good alternative to conventional high-pressure hydrogen storage vessels tank to their high hydrogen storage capacities and safety aspects [1]. Moreover, metal hydrides are potential candidates for other applications including gas purifiers, isotope separators, hydrogen sensors, thermal compressors, optical windows, Ni-MH batteries and more recently Li-ion batteries [2-3]. The pure magnesium reacts reversibly with hydrogen to form $MgH_2$. It is thus considered to be one of the most important candidates for the reversible storage of hydrogen due to its light weight, low cost and high hydrogen gravimetric density (7.6wt.%). However, its hydrogen ab*sorption*-desorption kinetics is unsatisfactory due to the very low diffusion of hydrogen in $MgH_2$ [4]. However, preparing nanocrystalline Mg by ball milling and adding transition metals [5- 7] or transition metal oxides [8] as catalysts improves the kinetics of material tremendously.

The studies of Mg-based hydrides with Al additions carried out [9–11] and another promising class of materials for hydrogen storage is the Al-based complex hydrides, Since Bogdanovic and Schwickardi showed that the decomposition of sodium alanate, NaAlH4, can be made reversible by the addition of Ti and Fe compounds as catalysts [12]. These studies stimulated the investigation of many other complex systems [13–16]. The addition of Al into Mg was inspired by several studies in recent review on the hydrogenation properties of Mg–Al alloys [17]. Which showed that the thermodynamics and kinetics of hydrogenation/dehydrogenation of Mg–Al alloys are generally improved compared to Mg alone.

This investigation inspired us to do compositional thin film fabrication approach to search new light-weight metal hydride storage materials. The ability to investigate hundreds of alloy compositions in a single thin film, the characterization of their microstructure before and after hydrogen loading and the determination of the most favorable kinetics enables us to optimize efficiently complex metal-hydride systems whose hydrogenation depends on a rapid interchange of thermodynamic stability, atomic diffusion of all constituents and surface catalysis.[18]. The optical band gap of bilayer calculated using Tauc relation [19]. The resistivities measurements of thin film hydride are carried out [20-23] and established the interaction of hydrogen with inter metallic as ionic model.

Hydrogen molecules and hydrogen-related defects in crystalline silicon was observed by Fukata et al [24] and neutralization of shallow acceptor levels in silicon by Atomic Hydrogen also observed by Pankove et al [25]. The behavior of hydrogen implanted during physical vapor deposition in Al, Mg and Mg-Al films were carried out by Milcius [26]and observed $MgH_2$ , $Mg(AlH_4)_2$, $AlH_3$ & $Al_2O_3$ peaks ,when films were plasma hydrogenated at different temperature. In magnesium alanate hydrides the Raman peaks found in stretching vibrations region between 1800 and 2000$cm^{-1}$and in fingerprint region between 600and 100$cm^{-1}$ observed by Fichtner et al [27].In this paper we are presenting first time electrical, optical and Raman spectroscopy studies of Mg/Al bilayer films including XRD. The changes were observed in optical band gap, electrical properties and Raman peaks with increasing hydrogen pressure.

## EXPERIMENTAL

Bilayer thin films of Mg/Al have been prepared by thermal evaporation technique. The Mg granules (99.99%) and Al foil (99.98%) were used for the present study. These materials were placed into two different tungsten boats in the vacuum chamber and then evaporated by resistive heating to prepared Mg/Al (Magnesium 200nm+Aluminium 200nm) bilayer thin films on glass and ITO substrates at pressure $10^{-5}$torr in chamber. After that prepared thin films were rapid thermal annealed (RTA) by Halogen light lamp (1000 W) to get homogeneous mixture of Mg/Al films. For this process, bilayer thin films were kept in quartz tube and then rapid thermal annealed by halogen light lamp(1000W) for 60 seconds. The Hydrogenation of Mg/Al bilayer has been performed by keeping these films in hydrogenation cell, where hydrogen gas was introduced at different pressure (30, 45 & 60 Psi) for half an hour.

Then UV–Vis absorption spectrums of these thin films are recorded at room temperature in the wavelength range of 300–900 nm with the help of Hitachi-330 spectrophotometer. X-ray diffraction measurements have been taken by using Panalytical System having Cu Kα, as a radiation source of wavelength $\lambda = 1.540598A°$ with $2\theta = 20^o$-$70^o$ at the scan speed $0.5^o$/min for the determination of structure. The analysis has been performed by using Powder X-ray Software. The transverse I-V characteristics of film samples have been recorded using Keithley-238 high current source unit and electrode contacts have been made using silver (Ag) paste on the thin films. I-V characteristics of thin film structure have been monitored with the help of SMU Sweep computer software. Raman spectra of annealed and hydrogenated Mg/Al bilayer thin films were taken by a continuous wave-Green laser with a constant wavelength 532 nm at room temperature by help of R-3000 Raman system. All the measurements have been performed at room temperature.

## RESULTS AND DISCUSSIONS

### Structrural Characteristics of Mg/Al Bilayer Thin Films

Fig. 1 shows the X-ray diffraction pattern of Mg/Al bilayer thin films with and without hydrogenation. In case of pristine film it is found that the diffraction peaks originate at $31.32^0$, $44.64^0$, $47.84^0$,$52.70^0$ and $67.02^0$ respectively correspond to planes (106), (405), (227), (512) and (526) for Mg/Al bilayer having lattice constant a= 11.38A and c= 17.87A in hexagonal structure. When thin film hydrogenated at 45 Psi hydrogen pressure ,then diffraction peaks are originate at angles $38.59^0$, $40.49^0$, $48.83^0$ and $64.45^0$ respectively, correspond to the planes (314), (225), (317) and (525) respectively of Mg/Al bilayer having hexagonal structure .we again hydrogenated this film at 60 psi then diffraction peaks are originate at 2θ angles of $40.32^0$, $45.62^0$, $48.75^0$ and $63.99^0$ respectively correspond to planes (008), (009), (317) and (517) having hexagonal structure without changing lattice constants.

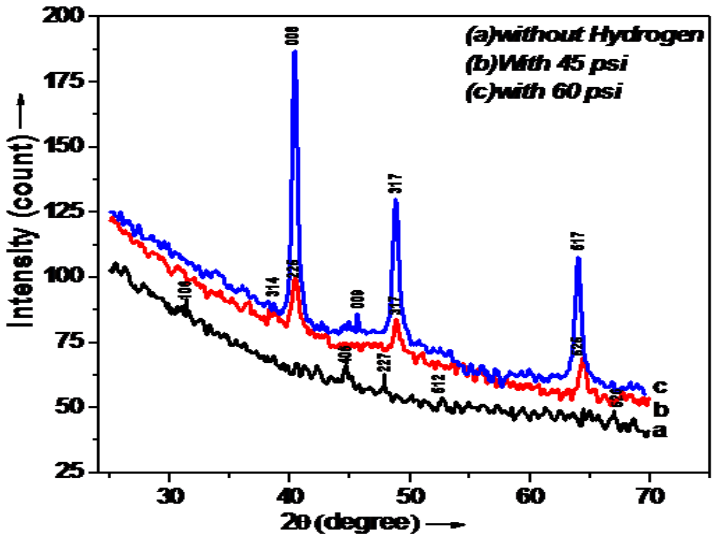


**Figure 1: XRD Pattern of the Mg/Al Bilayer Thin Films**

The XRD pattern of the Mg/Al bilayer thin film shows a hexagonal structure throughout hydrogenation process. However plane geometry of thin films has been found to change with hydrogenation that confirms the presence of hydrogen. We correlate small increase in peak at 45 Psi with molecular hydrogen absorption at interface of film and sharp intense peak at 60 Psi may be due to covalently bonded hydrogen with Mg/Al bilayer.

The crystallinity of films increases with hydrogen pressure may be due to formation of complex hydrides. The behavior of hydrogen plasma implanted during physical vapor deposition in Al,Mg and MgAl films were carried out by Milcius et al [26] using XRD and they had been observed $MgH_2$ , $Mg(AlH_4)_2$, $AlH_3$ & $Al_2O_3$ peaks ,when the films were plasma hydrogenated at different temperature. The few of peaks also approximate match with our results it may be due to our preparation process was differ by him. These results are confirmed latter in this paper by Raman spectroscopy.

### Optical Properties of Mg/Al Bilayer Thin Films

The optical absorption spectra's are shown in fig. 2(a) on different hydrogen pressure for Mg/Al films. These spectra showing that the absorption is decreased with hydrogen pressure. By studying absorption spectra of Mg/Al bilayer thin films, one can get very useful information about the optical energy gap and characteristics of optical transitions. The

optical band gaps are determined from the extrapolation of the plots between $(\alpha h\nu)^2$ Vs photon energy ($h\nu$) by using Tauc's relation [19]. In fig.2 (b) we have extrapolated the straight line portion of the curve to intercept the energy axis; the value of the band gap energy has been calculated. It is found that with increasing hydrogen pressure the optical band gap increases from 2.74 to 2.93 eV.

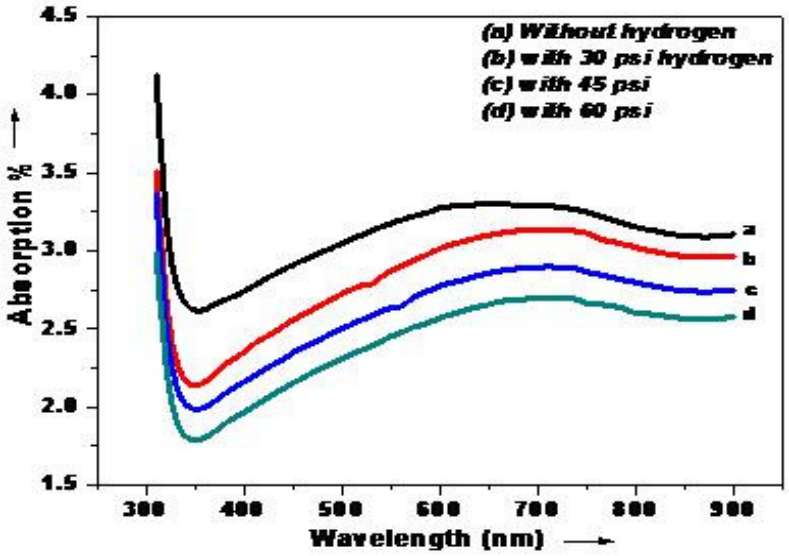


**Figure 2: (a) Absorption Spectra of Mg/Al Bilayer Thin Films**

The optical band gap increase can be explained on basis of two reasons: (i) The hydrogen concentration is increased, the film structure transforms from amorphous to the crystalline phase, which has a larger band gap than the amorphous one and (ii) It may be due to hydrogen accumulates at interface and takes electrons from the conduction band of thin film which support the anionic model of hydrogen interaction with inter-metallic [20-23].

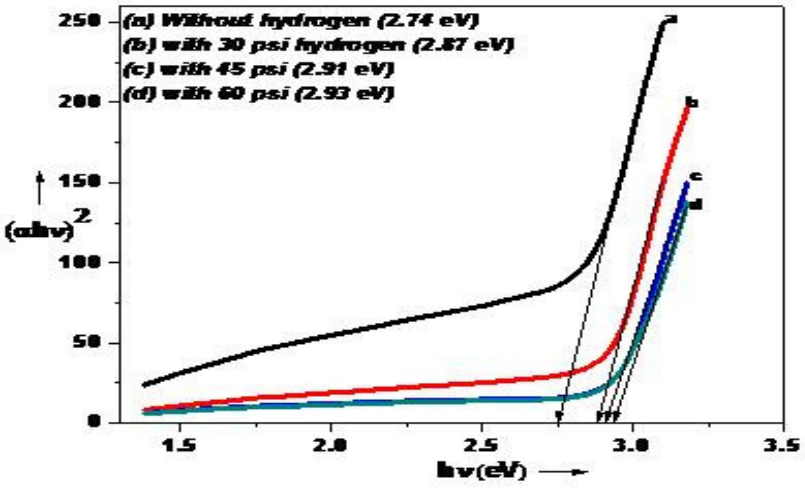


**Figure 2: (b) Optical Band Graph of Mg/Al Bilayer Thin Films**

**Electrical Properties of Mg/Al Bilayer Thin**

Fig.3 shows the I-V characteristics of Mg/Al bilayer thin films. Pristine bilayer shows ohmic behavior and after annealing it show partially non-ohmic indicating the possibility of mixing of bilayer structure at the interface.

The observed non linear behavior shows semiconducting nature of film with hydrogen pressure, it is due to hydrogenation of films that is already proved in this paper by increasing optical band gap with hydrogen pressure.

It means hydrogen takes electrons from the conduction bands during the hydrogen absorption process [23-25] and blocks the flow of charge carriers across the interface and so current decreases in forward as well as reverse direction. The conductivity of films then found to be decrease with hydrogenation.

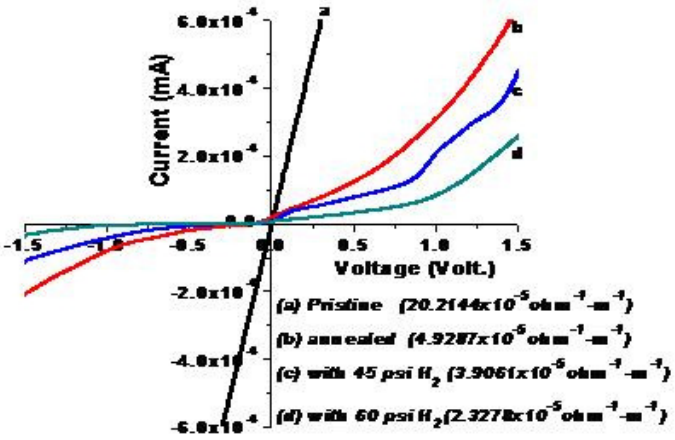


**Figure 3: I-V Characteristics of Mg/Al Bilayer Thin Films**

**Raman Spectroscopy**

Fig. 4 shows the variation in wave number versus intensity of Raman spectra. In these spectra we have observed three measure peaks at wave number 703.298, 1656.374 and 1785.317 $cm^{-1}$. In these spectra intensity of Raman peaks is decreased with hydrogenation with initial pressure 30 Psi corresponding to molecular hydrogen absorption at interface of bilayer and one can also note decrease in broadening of peaks on same pressure.

But in case of 45 Psi hydrogenation pressure the peaks intensity were found to be increase corresponding to covalently bonded hydrogen with Mg/Al bilayer film .It suggests that hydrogen may change the phase or make the bonding with metal interstitial as well as surface locations [25]. In case of magnesium alanate hydrides Raman peaks found in stretching vibrations region between 1800 and 2000$cm^{-1}$and in fingerprint region between 600and 100$cm^{-1}$ Fichtner et al [27]. Our results also originates the peaks in the same region it may be formation of complex hydride $Mg(AlH_4)_2$ and $MgH_2$.

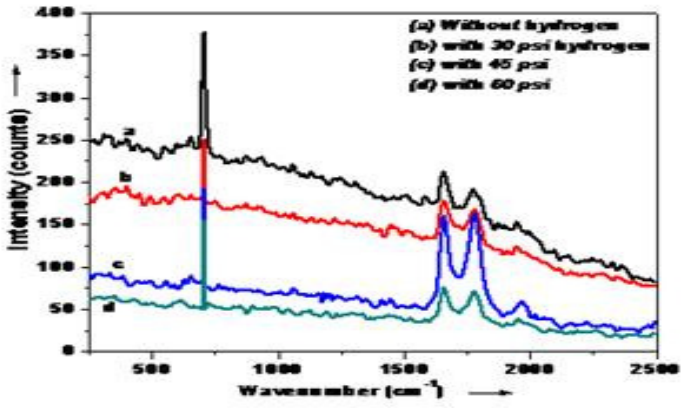


**Figure 4: Raman Spectra of Mg/Al Bilayer Thin Films**

## CONCLUSIONS

The hydrogen gas tailored the optical, electrical and structural properties of Mg/Al bilayer. The optical absorption decrease and optical band gap of thin films found to be increase with hydrogen pressure. XRD reveal hexagonal structure of annealed and hydrogenated Mg/Al bilayer thin film. I–V characteristics of as deposited thin films were found holmic behavior but after hydrogenation it found to be semiconducting.

Hence conductivity has been found to be decreased with hydrogen pressure that supports the increase in optical band gap. Increase in intensity of Raman peak suggested phase transformation or formation of complex hydrides. The enhanced hydrogen affinity at the bilayer film interface again suggesting that the study of complex hydride formation in thin films might give valuable information for the use of these Mg/Al bilayer thin film structures for hydrogen storage purpose for potable application and switchable mirrors.

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