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Study of Annealing and Hydrogenation Effect on Bilayer Mg-Co Thin Film by Thermal Vacuum Deposition

Dr. Mahesh K. Jangid

Department of Physics, Vivekananda Institute of Technology, Jaipur (India)

Abstract*—This article is reporting the effect of annealing and hydrogen on electrical properties of bilayer Mg/Co thin films. The thin films were prepared using thermal evaporation method at pressure 10-5 torr and Annealing of bilayer structure had been performed in vacuum at different constant temperatures for 1 hour and hydrogenated at pressure (40 psi) to see the effect of hydrogen. The I–V characteristics of pristine Mg-Co bilayer structure had been found to be ohmic behavior and current decreased with hydrogenation, where as the I–V characteristics of annealed samples show semiconductor behavior and the conductivity had been found to be increased with annealing temperature and decreased with hydrogenation. The Raman Spectroscopy data show that intensity of Raman peaks is decrease with hydrogen pressure.*

Keywords— Annealing, bilayer, hydrogenation, I–V characteristics, raman spectra, surface morphology.

I. INTRODUCTION

Metal hydride technologies have reached more practical and applied stages in recent years. The hydriding / dehydriding kinetics of metal hydrides are relevant to areas of design and applications of various metal hydride devices, especially in energy conversion devices such as heat pumps, refrigerators, automobiles, power generators, batteries and thermal energy storage units [1,2]. The structural and electronic state has intensively been investigated theoretically and experimentally for rare-earth hydrides, which show metal-insulator transitions with the opening of band gap by successive hydrogenation from di- to tri-hydride. The di-hydrides are excellent metals and shiny, while the tri-hydrides are insulators and transparent in the visible part of the optical spectrum In 1996, Huiberts et.al was discovered the amazing optical changes of yttrium and lanthanum upon the absorption of hydrogen. Several methods have been employed to overcome the kinetic limitation and thermodynamic stability of Mg-based hydrogen storage materials, including surface modifications addition of catalysts, and formation of metastable structures or multi-phase materials. Transition metals have shown good catalytic effects on hydrogen desorption of MgH2 after being mechanically milled with the hydride [3]. A very interesting development in the metal hydrides was found in 1995 by Huiberts [4] with the discovery of a spectacular change in the optical and electrical properties of thin films of Y and La hydrides near their metal–insulator transition as hydrogen is absorbed. These metals and their hydrides and dihydrides are shiny, while the trihydrides are large gap insulators, semi-transparent in the visible part of the spectrum. The possible applications of these materials extend to smart windows [5] and hydrogen sensors [6]. The study of these metal–insulator transitions has been extended now to intermetallic hydrides such as magnesium based alloys [7, 8]. Enache et al. [9] have investigated the electrical resistivity increases by almost three orders of magnitude between metallic Mg2Ni and transparent Mg2NiH4. Richardson et al.[10,11], discover that Mg based films absorb hydrogen very easily , While in bulk samples hydrogenation requires high temperatures (500 to 600 K) 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. This is especially important for applications. So far all alloys of Mg with the transition metals (TM) Ni, Co, Fe, Mn, V have been found to switch with hydrogen [12]. The electrical conductivity of CdTe semiconducting thin films prepared by physical vapor deposition onto unheated glass substrates was investigated by Rusu et al. and the conductivity has been found to ranged from 10-6 to 10-4 Ώ-1-m-1 [13,14]. The interaction of hydrogen in a metal hydride can be understood by using the anionic model [15]. In the present work have been studied the effect of annealing and hydrogenation on current-voltage characteristics, Raman spectra and surface morphology of Mg-Co bilayer structure.

II. EXPERIMENTAL

2.1 Sample preparation

The samples were prepared by thermal evaporation method using vacuum coating unit. The Hind High Vacuum unit was used for this purpose and vacuum chamber contains pressure of the order of 10^{-5}torr. Mg granules (99.999%) and Co powder (99.98%) pure were purchased from Alfa Aesar, Jonson Matthay Company, U.S.A. used for the present study, is placed into two different boats in the vacuum chamber. The glass substrates cleaned by plasma sputtering technique were placed in the substrate holder above the boats carrying materials; the source to substrate distance was kept 15 cm. The thin films of Mg-Co (Mg-206.47nm, Co-167.65nm) had been performed by stacked layer method in situ evaporation and prepare bilayer structure. The thickness of films is measured by Quartz crystal thickness monitor.

2.2 Annealing

The bilayer structures of Mg-Co were annealed using hind high vacuum chamber at a pressure of 10^{-5} torr for 1 h at different temperature (365 & 465K) to get homogeneous mixture and inter-diffusion of bilayer structures.

2.3 Hydrogenation

Hydrogenation of Mg-Co bilayer structure has been performed by keeping these in hydrogenation cell, where hydrogen gas was introduced at pressure 40 psi for half an hour. As pristine well as annealed bilayer structures were separately hydrogenated and termed as grown hydrogenated and annealed hydrogenated thin films respectively.

2.4 I-V characteristics

Transverse I-V characteristics of pristine hydrogenated and annealed hydrogenated samples have been recorded using Keithley-238 high current source measuring unit. The applied voltage was with 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 bilayer structure have been monitored with the help of SMU Sweep computer software. All the measurements have been performed at room temperature.

2.5 Raman Spectroscopy

Raman spectra of annealed and hydrogenated bilayer structure are taken by a continuous wave-Green laser with a constant wavelength 532 nm at room temperature by help of R-3000 Raman system.

2.6 Optical microscopy

The optical micrographs have been observed with the help of Labomed optical microscope at 10 x magnification having resolution of the order of 1 mm and the microscope was kept in reflection mode. The micrographs were stored in computer through standard software (Pixel View).

III. RESULTS AND DISCUSSION

3.1 Current- Voltage characteristics

Fig. 1 show that the I-V characteristics of pristine Mg-Co bilayer structure. It has been found to be ohmic and current is found to be increased with hydrogenation (TABLE). Therefore it may be attributed that hydrogen acts as a donor candidate and exhibits the charge transfer from hydrogen to bilayer structure as a result it may form a conducting bridge between the defect sites available in the bilayer structure.

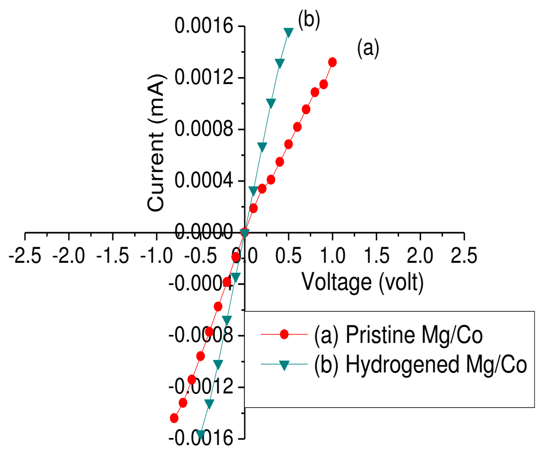

Fig.1 I-V characteristics of pristine and hydrogenated Mg-Co bilayer structure

TABLE: Conductivity Conductivity (10^{-4} Ω^{-1}-m^{-1}) of Mg-Co bilayer structure

Annealing Temp.	Conductivity (10^{-4} Ω^{-1}-m^{-1})	
	Without H_2	With H_2
Pristine	1.32	3.07
365 K	0.78	0.68
465 K	1.77	1.12

Fig. 2 show the effect of annealing on the bilayer structure indicating the possibility of mixing of bilayer structure at the interface showing the partially semiconducting nature and the conductivity has been found to be increased with annealing temperature (TABLE). There is a sufficient increase in current with increasing temperature; this may be due to the increase of grain size with increase of annealing temperature [16-18].

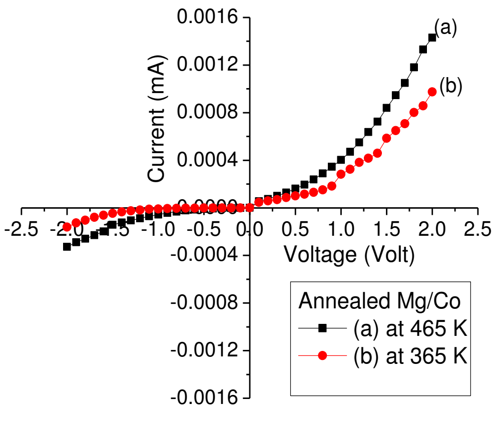

Fig. 2 I-V characteristics of annealed Mg-Co bilayer structure

Fig. 3 show the effect of hydrogen on annealed Mg-Co bilayer structure, the conductivity has been found to be decreased with hydrogenation (TABLE). It means hydrogen takes electrons from the conduction bands during the hydrogen absorption process and blocks the flow of charge carriers across the interface and current decreases in forward as well as reverse direction. The electronic passivation of host impurities induced by atomic hydrogen in semiconductor well agrees as reported by Pankove et al [19]. Hydrogen interacts with metals and semiconductors and takes electron from conduction band of metal as anionic model. This similar to our earlier work [20] this shows that the conductivity of CdTe/Mn semiconducting thin film has been found to be decreased with hydrogenation.

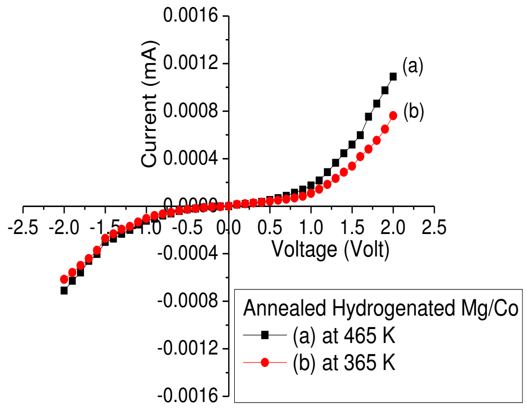

Fig. 3 I-V characteristics of annealed hydrogenated Mg-Co bilayer structure

3.2 Raman spectroscopy

Fig. 4 show the variation in intensity versus wave number of Raman spectroscopy. In these spectra intensity of Raman peaks is decreased with annealing and also decreasing with hydrogenation and also noted decrease in broadening of peak. It suggests that hydrogen may change the phase or make the bonding with metal interstitial as well as surface locations [21].

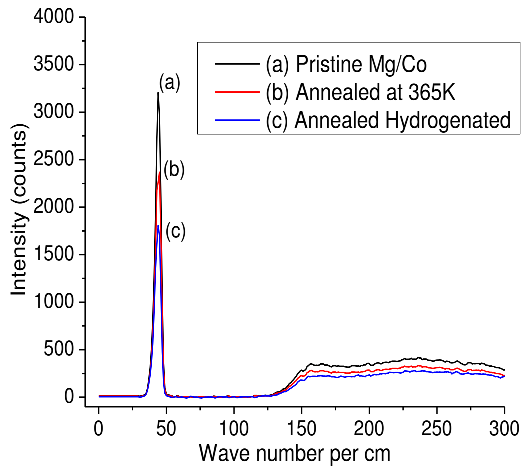

Fig. 4 Raman spectra of pristine, annealed and annealed hydrogenated Mg-Co bilayer structure.

3.3 Surface morphology

Fig. 5 show the optical surface morphology of pristine (a) and annealed at 365K (b) for Mg-Co bilayer structure. These are recorded in reflectance mode of optical microscope. We have observed slightly color change due to hydrogenation.

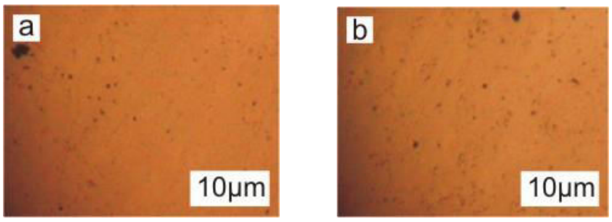

Fig. 5 The optical micrographs of Mg-Co bilayer structure (a) pristine and (b) annealed at 365K

IV. CONCLUSIONS

Hydrogen is tailored the electrical properties of bilayer Mg-Co thin film. It is concluded from the above study that I–V characteristics of pristine Mg-Co bilayer structure have been found to be ohmic behavior and current has been found to be decreased with hydrogenation, where as the I–V characteristics of annealed samples show semiconductor behavior and the conductivity has been found to be increased with annealing temperature and the conductivity has been found to be decreased with hydrogenation. In Raman Spectroscopy intensity of Raman peaks is decreases with hydrogen pressure that suggesting that hydrogenation may change the structural phase. Decrease in intensity of Raman peak may be due to phase transformation. Surface topography confirms the uniform deposition and proper mixing of bilayer structure. These results indicate that these bilayer structures can be used to hydrogen storage purpose.

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