ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 10, No. 3. 2004

Behavior of Hydrogen Implanted during Physical Vapor Deposition in Al, Mg and MgAl Films

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Received 25 June 2003; accepted 15 September 2004

The behavior of hydrogen in Mg, Al and MgAl thin films on stainless steel substrate was investigated in this work. The hydrogen ions extracted from plasma were used to load hydrogen into the film material. Glow discharge optical emission spectroscopy (GDOES) was applied to obtain the hydrogen depth profiles in Al films versus hydrogenation parameters. The MgH_2, AlH_3 and $Mg(AlH_4)_2$ hydrides were identified in plasma hydrogenated at temperature below 100 °C films using X-ray diffraction (XRD). The reversible hydride phase transformation has been observed at elevated temperatures. Three hydrogen release stages at 100, 130 and 400 °C were registered for $Mg(AlH_4)_2$ corresponding to three steps of decomposition.

Keywords: Al, Mg, MgAl, hydrogenation, synthesis, hydrides, decomposition.

1. INTRODUCTION

Mobile applications in combination with hydrogen fuel cell systems require sustainable storage materials that contain large amount of hydrogen. Furthermore, low decomposition temperatures and fast kinetics for adsorption and desorption of hydrogen are required. Numerous hydrides with metallic bonding (e.g., those represented by $LaNi_5$ and TiFe) have been developed to reversibly store hydrogen at near-ambient temperatures, but they suffer from poor gravimetric capacity (typically less than 2 wt.% H). At the other extreme, there are ionic and covalent bonded hydrides (e.g., Li and Mg based alloys, respectively) that have good gravimetric capacities (5 – 10 wt.% H), but require high temperatures (> 420 K) to release the stored hydrogen at positive pressure [1].

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.

Thin film physical vapor deposition technologies allow applying nontraditional and new nanotechnology methods for designing high performance hydrogen storage materials. Hydrogen can be introduced in strictly controlled manner into the growing film employing simultaneous deposition and hydrogen ion irradiation technique. Additional ion bombardment during film growth modifies new phases synthesis kinetics.

The growing film under controllable ion irradiation contains many grain boundaries, defects, disorder or strain. These materials are not thermodynamically stable, such as amorphous or nanocrystalline metastable phases, although very often exhibiting stable and reproducible behavior in practical applications. The adsorption – desorption properties of these materials cannot be fully described by the basic thermodynamic functions, so that P-C isotherms can differ significantly from theoretical expectations. In nanocrystalline materials a rather large fraction of hydrogen atoms can be weakly trapped in the region of the grain boundaries.

Aluminum dissolves hydrogen in only very small quantities, approximately 1 ppm at. near the melting point at atmospheric pressure [2]. When the hydrogen content in the Al film is far from the equilibrium value, as a consequence of ion implantation processes, the behavior of H atoms is strongly related to crystalline defects.

The hydrogen solubility in magnesium at room temperature is 2 – 3 orders of magnitude higher than in aluminum [3].

In this paper, the behavior of hydrogen, implanted during deposition of Al and Mg films, is studied by glow discharge optical emission spectroscopy (GDOES) analysis technique. Hydrogen-related phase transformation is studied by X-ray diffraction (XRD), and the surface topography is observed by scanning electron microscopy (SEM). The correlation between the changes of physical structure and chemical features is shown. The aim of this work is to reveal how different H-trapping properties of two metals affect different behavior of hydrogen.

2. EXPERIMENTAL

1 – 7 μm-thick pure Al and Mg thin films were deposited at room temperature on (100) oriented silicon wafers by dc magnetron sputtering (nominal target purity better than 99.99 at.%) in a vacuum chamber with the Ar gas working pressure 0.4 Pa. The deposition rate of Mg film was 2.2 nm/s and Al film – 4.4 nm/s. Hydrogenation of these films was carried out in hydrogen plasma: ion current 20 – 200 mA; temperature up to 200 °C.

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1 – 7 μm-thick hydrogen saturated Al and Mg thin films were deposited at room temperature on (100) oriented silicon wafers by dc magnetron sputtering in vacuum chamber with the $(Ar+H_2)$ gas working pressure 0.2 – 0.4 Pa. The ratio of partial pressure of H_2 gas to Ar gas was about 10. The MgAl alloy films were grown by co-deposition of Mg and Al atoms arriving from two independent magnetrons. The growing film was bombarded by Ar and H ions extracted from plasma under the negative bias voltage equal to 100 V. The ion current density directed to the growing film was varied in the range 0.1 – 2 $mA \cdot cm^{-2}$.

The concentration of hydrogen in the growing film was calculated on the basis of the simulation of simultaneous action of processes of adsorption, sputtering and hydrogen implantation [4, 5]. It is in complex dependence on the adsorption and sputtering rates and the flux of incident hydrogen atoms and molecules. For the hydride synthesis, high concentration of accommodated hydrogen in growing film is necessary. It has been realized in regime of low film growth, which is defined by deposition and sputtering rates. Synthesis of magnesium alanate requires the ratio of atomic concentrations as Mg : Al : H = 1 : 2 : 8.

In the present work the microstructure of films was analyzed by X-ray diffraction with the 2Θ angle in the range 20 – 70° using CuK_α radiation in steps of 0.05°. Peak positions and full width of peak at half maximum of intensity were obtained by fitting the measured peaks with two Gaussian curves in order to find the true peak position and width corresponding to monochromatic $K_{\alpha 1}$ radiation. The average crystallite dimension of films, D, was calculated using the formula $D = 0.9\,\lambda\,(\beta \cos\Theta)^{-1}$ neglecting the microstrain, where λ is the X-ray wavelength, Θ is the Bragg diffraction angle and β is the full-width of the peak after correcting for the instrument broadening. The identification of phases has been performed using Crystallographic Search-Match program.

3. RESULTS

3.1. Hydrogen in Al thin films

Fig. 1 shows the GDOES depth profiles of hydrogen atoms implanted during film deposition for different ion current densities extracted from plasma under negative 100 V bias voltage. It is seen that the depth profiles of accommodated hydrogen depends on the ratio of fluxes of arriving Al atoms and incident ions. The film surface is enriched with hydrogen atoms, which can be included in OH groups and water. Non-hydrogenated Al film shows small amount of H atoms homogeneously distributed across the thickness except the near surface region.

From the XRD study, crystal structure changes were observed for the variation of the hydrogen concentration in film. Fig. 2 includes XRD patterns of non-hydrogenated Al film and of Al film saturated up to 80 at.% of H at temperature 70 °C. The XRD pattern of the non-hydrogenated Al film displays only Al(111) reflection. The estimated grain size using Debye-Scherrer analysis is equal to 22 – 30 nm. When the hydrogen concentration in Al film exceeds 20 – 30 at.% the diffraction peak for aluminum hydride (AlH_3) is identified at $2\Theta = 33.1°$. It indicates that AlH_3 phase is formed with the mean size of crystallites 32 – 36 nm in the matrix of Al film. The strain is necessary for the material equilibrium in the presence of two phases. This strain is unhomogeneous over the film volume and broadens Al reflection.

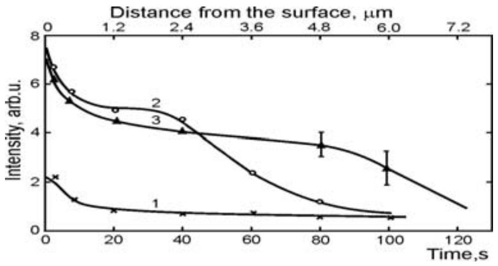

Fig. 1. Hydrogen distribution profiles in Al films after hydrogenation at 100 °C for 30 min and different ion currents equal to 0 (non-hydrogenated), 0.6 $mA \cdot cm^{-2}$ and 1.2 $mA \cdot cm^{-2}$, curves 1 – 3, respectively

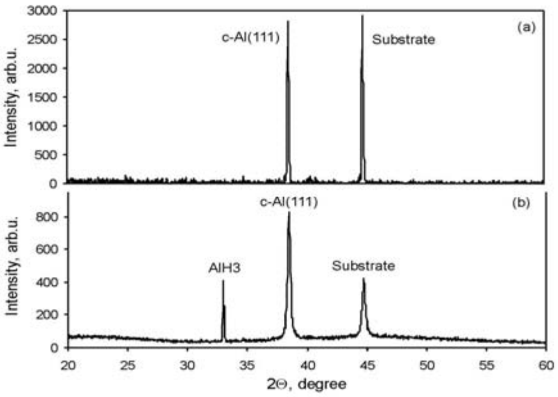

Fig. 2. The XRD patterns for non-hydrogenated (a) and hydrogenated at 70 °C for 30 min (b) films

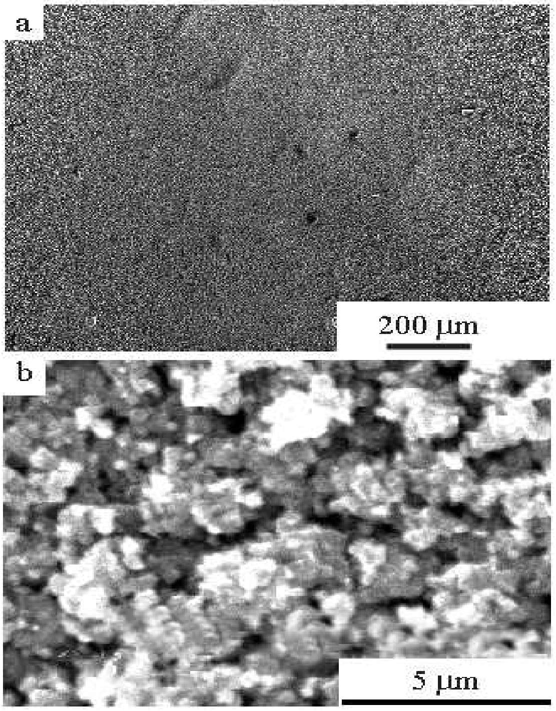

Fig. 3. The SEM surface views of as-deposited (a) and hydrogenated at 70 °C during deposition (b) Al films

The SEM photographs showing the topography of the non-hydrogenated and hydrogenated Al films are included in Fig. 3 a and b in correspondence to the XRD results presented in Fig. 2 a and b, respectively. The topography of non-hydrogenated Al film is smooth and homogeneous. The hydrogenated Al film becomes unhomogeneous in plane and the clusters 5 – 10 μm diameter are observed which have been identified as clusters of nanocrystallites.

3.2. Hydrogen in Mg thin films

Fig. 4 shows the XRD patterns of Mg film deposited without simultaneous incorporation of hydrogen (Fig. 4 a) and for different ion current densities extracted from Ar plasma during film growth. We can see Mg(002), Mg(101) and Mg(004) peaks from the Mg film, which was grown in pure Ar working gas.

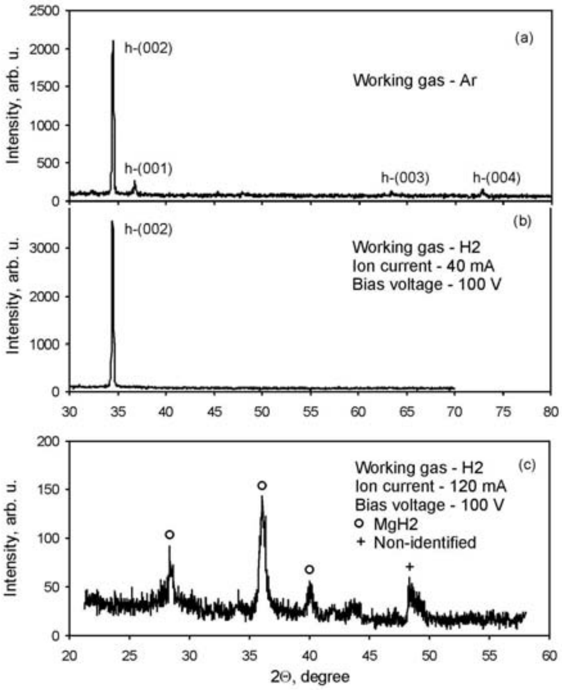

Fig. 4. The XRD patterns of Mg films: a – non-hydrided, b – after hydrogenation under irradiation for different ion currents – 40 mA (b) and 120 mA (c)

The XRD profiles reveal that Mg grains epitaxially prefer the c-axis orientation. The introduction of small quantities of hydrogen in the growing film modifies the structure of grown film. The other peaks except Mg(002) disappear, the mean grain size decreases from 80 – 120 nm for non-hydrogenated Mg film up to 30 – 40 nm for hydrogenated one. When the concentration of hydrogen reaches about 10 – 20 at.%, the diffraction peaks for magnesium hydride (MgH) at $2\Theta = 48.1^{\circ}$ and magnesium dehydride (MgH_2) at $2\Theta = 28^{\circ}$, 36.5° and 40.5° appear in the diagram. With the further increase in hydrogen concentration the MgH peak decreases and the MgH_2 peaks grow. It is noteworthy, the measured positions of MgH_2 peaks are shifted to the database values 26.8°, 35.4° and 40.1°, respectively. This means that the lattice plane distance is changed and MgH_2 phase may not swell to its equilibrium value.

On the basis of the evolution of the amplitude of MgH and MgH_2 peaks in XRD patterns, the fractional volume of MgH_2 phase in the Mg film in dependence on the ion current density directed to the growing film density (Fig. 5) has been obtained. It is seen that the full transformation of Mg film into MgH_2 takes place at ion current density equal to about 10 $mA \cdot cm^{-2}$.

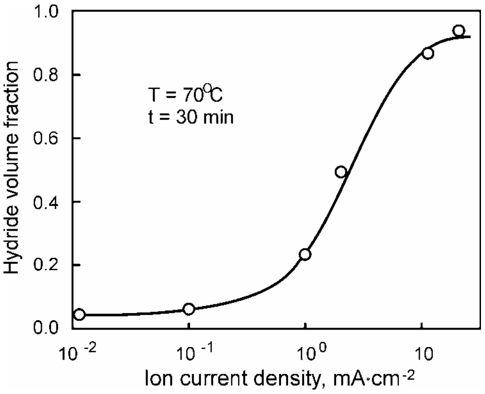

Fig. 5. The dependence of the fractional volume of MgH2 phase in Mg film after hydrogenation at 70 ºC for 30 min in dependence on the ion current density

Therefore, at low hydrogen concentration in Mg film, the hydrogen atoms dissolve in the lattice interstice as solid solution [6]. Almost no hydride was found in the samples with hydrogen concentration below 10 at.%. At a higher concentration, the chemical effects become observable, then hydrogen atoms are bound in lattice. SEM analysis of the hydrogenated Mg films have not evidenced the pronounced variation in surface topography.

3.3. Hydrogen in MgAl thin films

The XRD patterns of MgAl films hydrogenated during deposition are shown in Fig. 6.

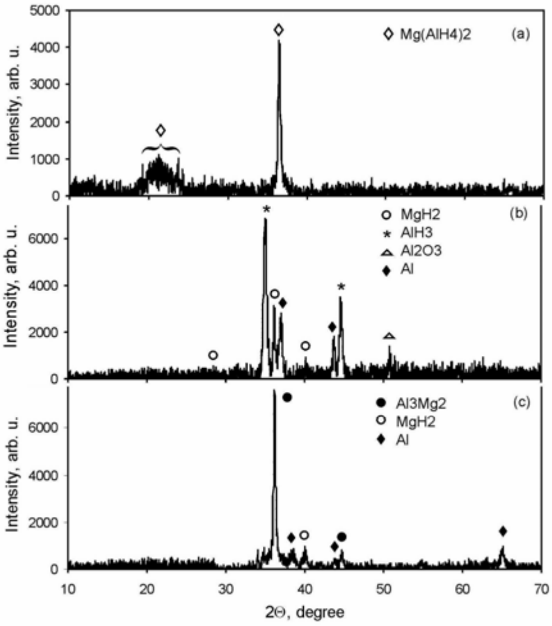

Fig. 6. The XRD patterns of MgAl films hydrogenated at different temperatures: a – 100 ºC, b – 130 ºC and c – 200 ºC

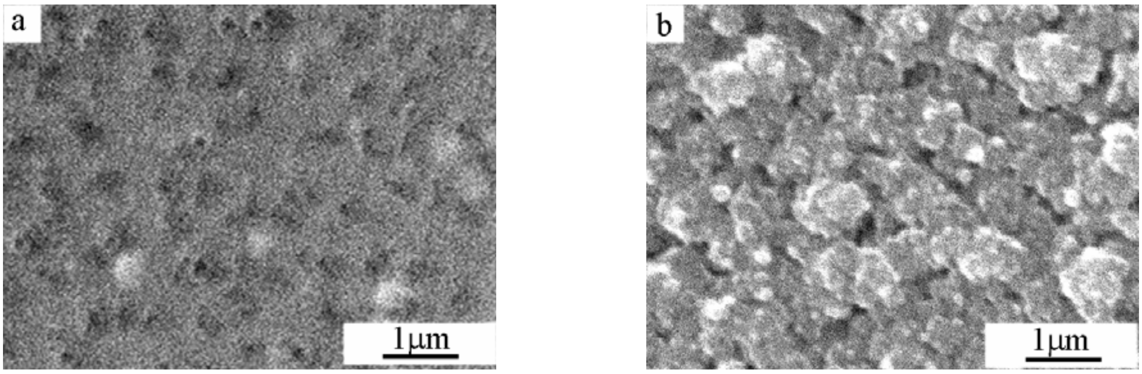

Fig. 7. The SEM surface views of MgAl films hydrogenated at 30 ºC – (a) and 180 ºC – (b)

The $Mg(AlH_4)_2$ compound is identified at synthesis temperatures less than 100 ºC (Fig. 6 a). The plasma – enhanced synthesis reaction takes place as

$$Mg + 2Al + 8H \rightarrow Mg(AlH_4)_2 \qquad (1)$$

The thermal treatment of hydrogenated films changes their XRD patterns, as it is seen in Fig. 6 b and c. Three-step transition can be identified.

The first step of the decomposition takes place in the temperature range 110 – 150 ºC

$$Mg(AlH_4)_2 \rightarrow MgH_2 + 2AlH_3 \qquad (2)$$

magnesium and aluminum hydrides are formed. The second step starts at temperature above 150 ºC, when decomposition of alane (AlH_3) phase starts as $2AlH_3 \rightarrow 2Al + 3H_2$.

Further increasing the treatment temperature above 400 ºC the decomposition of magnesium hydride goes as $MgH_2 \rightarrow Mg + H_2$.

The Al released from the second step and Mg released from the third step precipitate and intermetallic compound Al_3Mg_2 is formed as $4Al + 2Mg \rightarrow Al_3Mg_2 + Al$.

The SEM surface view of as synthesized $Mg(AlH_4)_2$ films are shown in Fig. 7 for the following parameters of hydrogenation: ion current 40 mA, temperature 30ºC – (a), and ion current – 120 mA, temperature 180 ºC – (b).

4. CONCLUSIONS

Mg and Al films were saturated with hydrogen atoms/molecules during their vapor deposition in hydrogen plasma under the negative bias voltage at temperature below 100 ºC. In all cases the synthesis of hydrides was observed using XRD analysis. The release of hydrogen follows the decomposition of synthesized hydrides. The decomposition of MgH_2 has been observed at 400 ºC, the decomposition of AlH_3 at 130 ºC and the three step decomposition of $Mg(AlH_4)_2$ at 100 ºC, 130 ºC and 400 ºC, respectively. The hydrogen atoms released after decomposition of MgH_2 thin films are effused out through the surface and the desorption kinetics is probably controlled by surface recombination process. The hydrogen atoms released after decomposition of AlH_3 and $Mg(AlH_4)_2$ phases are contained mostly as H_2 molecules in bubbles. Hydrogen atoms effusion is controlled by their transport through the thin natural Al_2O_3 oxide layer, mainly by lifting the cover of bubble.

Acknowledgments

The work was supported by the Sandia National Laboratories (USA). Authors express special gratitude for Mr. A. Vasys (USA) for the encouragement and help in an administration of the research, and wish to thank Prof. Liudvikas Pranevicius for helpful discussions.

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DOI: 10.5755/j02.ms.26631