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Thermodynamics of hydrogen uptake in Mg films studied by resistance measurements

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Abstract

Resistance measurements were done on 100 nm thin magnesium films covered with 10 nm palladium in temperatures ranging from 60 to 100 °C. The samples were grown by dc sputtering system with a base pressure of $\sim 10^{-6}$ mbar. The measurements were done in situ in the sputtering chamber where the samples where grown, without breaking the vacuum so as to minimize contamination. Results show similar thermodynamic behavior to that found in bulk samples and samples made by ball milling. Resistance measurements of thin films could therefore be a useful tool in screening for changes in the binding energy of hydrogen in alloyed thin Mg films. Owing to the significantly lower loading times of thin films at this temperature range, a wide range of new materials consisting of nanoscale structures of Mg and other elements can be produced through sputtering and studied with the equipment.

Keywords: Thin films; Hydrogen; Magnesium

Currently, there is considerable amount of interest in metal/hydrogen systems. This interest is mainly due to the high storage capacity of metal hydrides. Magnesium is one of the lightest storage material known, it is abundant and inexpensive. The main problem with using magnesium as a storage material for hydrogen, is the high binding energy of hydrogen in magnesium, since it desorps hydrogen at the high temperature of 300 °C . The aim of this work was to develop an instrument and experimental methods using thin films to find new magnesium based materials for hydrogen storage. Thin films offer an opportunity to grow new samples fast with novel structures. Sequential growing layers of different materials with thicknesses in nanometer dimensions on a substrate results in fast alloy preparation or new materials with amorphous structures.

A UHV sputter deposition system with three magnetron sources has been built to grow such thin film structures. To study the hydrogen uptake and the thermodynamic properties of the new materials four point resistance measurements are used. The four point probe measurement is a well known method to study the properties of conducting thin films. Under applied hydrogen pressure the resistance of a sample that absorbs hydrogen increases. If the hydrogen pressure is increased gradually in steps at constant temperature, the resistance change is a measure of the hydrogen concentration in the sample.

The sputter chamber was fitted with a sample holder containing the four point probe setup. Therefore, the resistance measurement can be performed in situ after the growth and contamination from water and oxygen is minimized. The sample holder also adds the possibility to measure the resistance of the film as it develops during growth. The thermal stability or alloying behavior of the grown structure can then be studied by thermally cycling the sample. Irreversible resistance change during thermal cycle indicates diffusion or phase separation of certain elements in the film.

In this article, pure magnesium is used to characterize the function of the growth instrument and sample holder. The layout of the sample holder and masks can be seen in Fig. 1. There the sample is grown in two stages. First two 30 nm palladium contact pads are grown through a mask on each end of

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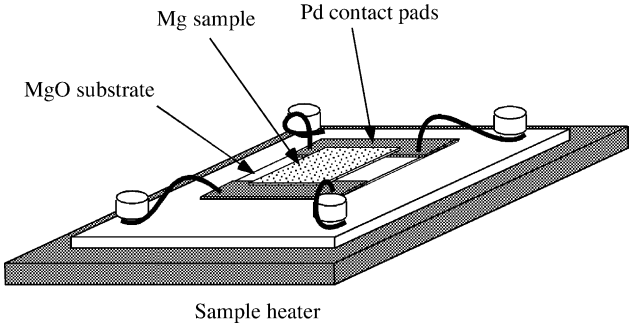

Fig. 1. The drawing shows the design of the sample holder with the four point probe for resistance measurements and the two growth masks.

the 10 mm × 5 mm (0 0 1) oriented polished MgO substrate. Then the Mg layer is grown through another mask on top of the contact pads. Finally, a capping palladium overlayer is grown on top to catalyze dissociation of hydrogen molecules on the surface. Electrical current of 1.0 mA is sent through the sample by two of the contact wires while the voltage drop across the sample is measured by the other two.

Fig. 2 shows the growth curve of the magnesium sample. The four point resistance measurements is used to monitor both the growth and the stability of the Mg films. The plot shows well how the initial conductivity through the few atomic layer thick Mg film develops when the flow of Mg atoms starts to land on the substrate. The initial resistance change is slow indicating three dimensional growth of Mg islands on the MgO substrate. This plot also shows well that the structure of the film is changing slowly with time after growth. Half way through the growth period the growth is interrupted, this can be seen in the figure as a resistance increased indicating surface and structure change.

When the thickness of the sample has been obtained and the growth rate estimated the timescale axis in this graph

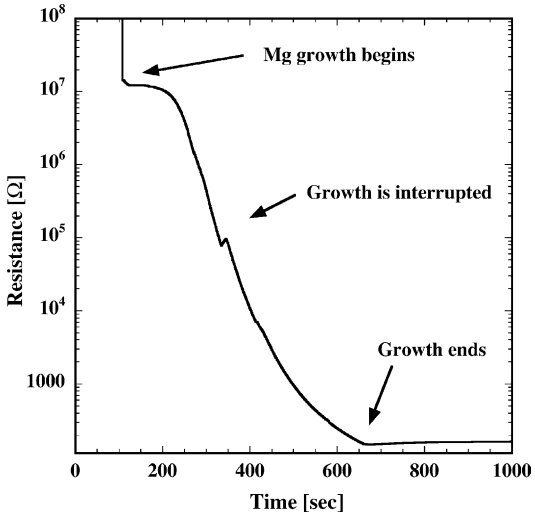

Fig. 2. The plot shows the resistance growth curve for a 100 nm Mg film capped with 10 nm Pd overlayer.

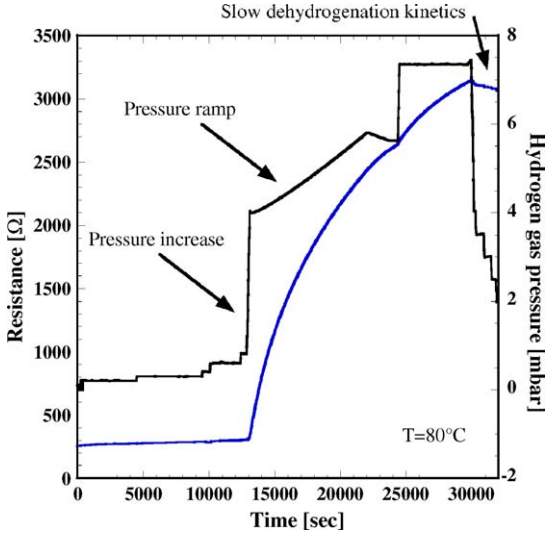

Fig. 3. The plot shows hydrogenation kinetics at low hydrogen concentrations. Fast kinetics and slow kinetics are visible in the film.

can be changed and the thickness of the film put there instead. The sample show no XRD reflection peak indicating nanocrystallinity and presence of great number of defects and grain bondaries.

Fig. 3 shows the kinetics of hydrogen uptake at $T = 80\,^{\circ}\mathrm{C}$. The pressure is increased in steps and the resistance change is monitored. The response to pressure increase is showing a fast and a slow behavior. At this temperature the bulk Mg has a phase transformation hydrogenation pressure of 0.11 mbar which is higher than the pressure used here. The hydrogen should therefore enter the low concentration α-phase of the 100 nm Mg layer or the Pd contact layers. The fast resistance increase indicates that hydrogen can enter all parts of the sample relatively fast. The slow kinetics in the resistance change is indicating that slow structural relaxation is occurring. The repeatability of the measurement is therefore not good as in the case of a crystalline film. The initial resistance value had increased in the range of 5–10% when the hydrogen was removed. At higher pressures the fast response is not observed indicating phase transformation to MgH_2 hydride phase.

Bulk magnesium initially forms a low concentration α-phase that develops into a high concentration metal hydride phase (MgH_2) at higher pressures. This hydride is an insulator with a very high resistance. The binding energy (ΔH) of the α-phase is −0.05 eV/atom, while the magnesium hydride phase MgH_2 has a value of −0.37 eV/atom [1,2]. The hydrogen uptake of thin magnesium films covered with palladium have been studied with nuclear reaction analysis (NRA) and quartz crystal microbalance (QCM) methods [3,4]. The main findings using the hydrogen profiling method were the formation of surface hydride MgH_2. The mobility of hydrogen through this surface hydride was found to be very low As the hydride phase forms in the palladium magnesium interface, transport of hydrogen deeper into the sample is slowed down.

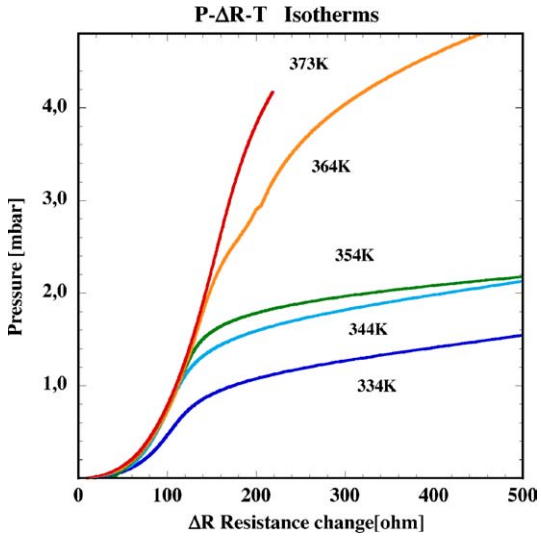

Fig. 4. The resistance isotherms for the 100 nm Mg film.

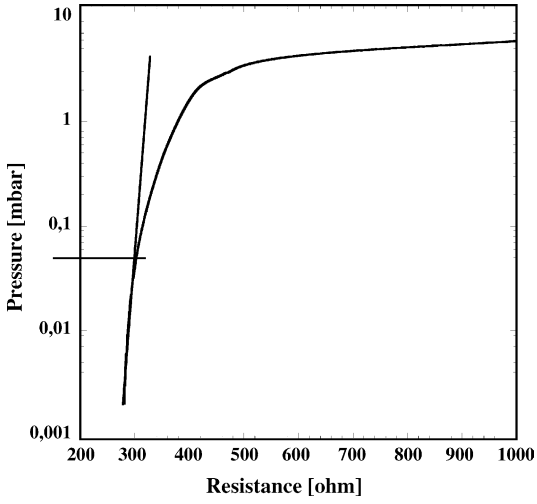

Fig. 5. Plateau pressure determination by observing the change in resistance behavior.

In this work, resistance measurements were used to monitor the hydrogen uptake of thin magnesium films covered with palladium. Interface hydride is expected to be formed and since the the hydride is an insulator the resistivity increases in proportion to the ratio of the sample reacted. However, in the low concentration α-phase the hydrogen atoms are very mobile and the sample is conducting, therefore the resistance gives good indication of the hydrogen concentration in the film. Two methods are therefore needed to calibrate the resistance isotherms into concentration isotherm.

This behavior is clearly seen in the measured resistance isotherms presented in Fig. 4, where the low concentration phase is characterized by a region of small resistance changes while hydride formation results in a large resistance change. It is difficult to obtain thermodynamic information from the resistance isotherms since information of absolute hydrogen concentration is lacking. However, if the plateau pressure for the formation of the MgH_2 hydride can be observed the binding energy (ΔH) of the MgH_2 is obtained using Vant Hoff plots. Information of hydrogen concentration is not needed. In the resistance isotherms the plateau pressure is not seen but when hydride formation starts the resistance change is expected to increase much faster.

Fig. 5 shows this behavior very well. The plateau pressure is determined when the relationship between resistance and log(pressure) deviated from linear behavior. Sieverts like plot, log(pressure) versus log R (log concentration), is therefore not linear. That indicates that heat of solution is changing as more hydrogen is added to the sample at low hydrogen concentration. But that is characteristic of defect and interface occupation of hydrogen. The plateau pressure analysis was done for the four temperatures and the results are shown in Fig. 6. In same plot the values for bulk magnesium is plotted for comparison.

The slope of the plotted plateau pressure in Fig. 3 then gives the ΔH from which the binding energy of the hydrogen can be obtained. According to these results, the binding energy of hydrogen in our film is larger than for the bulk magnesium. However, the uncertainty in the plateau pressure determination is still considerable due to the inherent slow kinetics of hydrogen transport and hydride formation of the Mg film.

Experimental apparatus to grow thin film samples and measure the hydrogen uptake in situ has been built. This equipment was used with magnesium films with palladium capping layer and the resistance isotherms measured at different temperatures and pressures. The binding energy of the hydrogen in the magnesium hydride MgH_2 was found to be similar as that of bulk within the experimental error of the measurement data and methods used here. Future work will

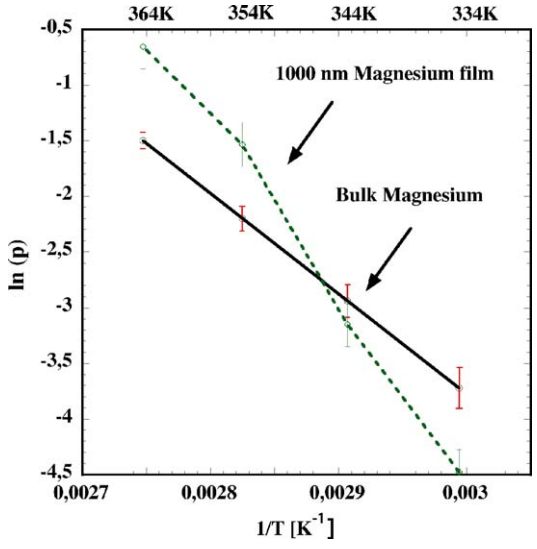

Fig. 6. Vant Hoff plot for magnesium bulk and the 100 nm Mg film the plateau pressure is plotted as function of 1/T.

aim to increase the kinetics and hydride formation in the Mg film by growing special samples with thinner Mg layers and possibly hydrogen transport layers.

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