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Resistivity and hydrogen uptake measurements in evaporated Mg films at 350 K

P. Hjort, A. Krozer*, B. Kasemo

Department of Applied Physics, Chalmers University of Technology, 412 96 Göteborg, Sweden

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Abstract

Resistivity measurements were performed during hydriding-decomposition cycles of UHV-prepared Mg films. The hydrogen exposures were made *in situ* at $p_{H_2} = 0.6$ torr and 350 K. To obtain measurable uptake rates at these conditions a thin layer of Pd (≈ 7 nm) was deposited on top of the typically 380 nm thick Mg films. Mg and Pd film thicknesses and hydrogen uptakes were determined by the frequency shift of a quartz crystal microbalance (QCM). Both the QCM and the quartz substrate onto which the Mg resistor film was deposited were mounted on the same sample holder. The p, T conditions were chosen so that hydrogen was distributed nearly homogeneously through the sample. The total hydrogen uptakes were in most cases kept small (<40 at.% H) to minimize the morphology changes.

The resistivity vs. H concentration relation is, within experimental uncertainty, linear up to $x = (H/Mg) \approx 0.4$ according to the formula $\rho(x) = \rho(0)(1 + c \cdot x)$, $c = 1.08 \pm 0.25$. The relatively large uncertainty is caused by a spread in the uptake data and by the irreversible resistance changes during hydriding-decomposition cycles. Both these uncertainties could be attributed to morphological changes induced by the volume expansion-contraction accompanying the cycles.

Exploratory measurements were also made at much larger H uptakes. These measurements reveal a rapid reversible resistivity increase at $(H/Mg) \approx 1.2$, which can be qualitatively attributed to the metal-insulator transition expected for the Mg-H_x system when the hydride phase becomes continuous. The measurements and their quantitative interpretation were complicated by the morphological changes of the sample(s) caused by volume expansion-contraction.

Keywords: Magnesium hydride resistivity; Metal-insulator transition

1. Introduction

There are several reasons to study how the resistivity of Mg is affected by hydrogen during hydriding and decomposition cycles. (i) Resistivity measurements may after calibration be used to detect the H concentration in Mg samples and can thus provide information about the hydrogen absorption-desorption kinetics and Mg-H₂ phase diagram. (ii) Resistivity changes upon hydrogen absorption (decomposition) contain information about hydrogen-induced changes of electronic properties as well as structural information on the hydride growth (decomposition). (iii) For the MgH_x system one expects a rapid increase of resistivity at the metal-insulator transition since MgH₂ is an insulator.

There are to our knowledge only two articles that

deal with resistivity measurements of the Mg-H₂ system [1, 2]. Hydrogen absorption was in [1] performed at high pressures ($>2 \times 10^3$ torr) and at temperatures $>100^\circ\text{C}$. The second article [2] describes a somewhat unusual system where hydrogen was introduced into Mg by implantation at low temperatures ($10\text{ K} < T < 100\text{ K}$). According to the authors the ultimate H/Mg ratio reached was around 1, although H fluences in excess of $H/Mg \approx 3$ were used. No hint of a structural phase transformation that accompanies the formation of Mg hydride was detected by TEM measurement. The authors believed an oversaturated α -phase of the Mg-H₂ system to have formed.

The scarcity of data for the MgH_x system over a wide range of temperatures and hydrogen contents is mainly due to the experimental difficulties encountered when trying to hydride Mg. The hydriding of Mg is extremely slow, also at high p and T [3], and concentration gradients are often likely to arise within

* Corresponding author. E-mail: krozer@fy.chalmers.se.

the sample [3,4]. To catalyze hydrogen dissociation we have covered our UHV-evaporated Mg samples with an evaporated thin Pd layer on top. Moreover Mg (like most other metals) tends to disintegrate due to volume expansion and accompanying crack formation upon hydriding. Sample disintegration affects both the resistivity measurements and the concentration measurements. The effect of changing sample morphology on resistivity is rather obvious. It is difficult however to separate experimentally the hydrogen embrittlement-induced changes of resistivity from the resistivity changes due to hydrogen absorption.

Previous results [4,5] on the kinetics of hydrogen uptake have shown qualitatively that concentration gradients increase with the “distance” from the phase boundary in the p , T space, p_{pl} and T_{pl} ; the larger the difference $p - p_{\text{pl}}$ is, at a given T_{pl} , the more the hydrogen distribution varies. To minimize hydrogen concentration gradients we have therefore performed experiments at pressures and temperatures as close to the phase transition region as possible.

2. Experimental

The experiments were performed in a system described in detail elsewhere [5,6]. It consists of a UHV chamber with facilities for Mg and Pd evaporation, auger electron spectroscopy (AES) for surface purity and composition control and mass spectrometry for composition measurements. The system has an attached high pressure cell, into which the sample can be transferred under maintained UHV conditions.

Uptake-decomposition measurements were done using a QCM device, or volumetrically. The latter measurements were performed by monitoring the hydrogen pressure decrease to typically 10% of the total pressure during uptake experiments, with the high pressure cell valved off. After the 10% pressure decrease was reached, new gas would be admitted into the cell. Volumetric measurements required volume calibration of the high pressure cell compartment ($\approx 85 \pm 25$ ml).

For the present work we have modified the sample holder to contain a quartz glass substrate for deposition of the Mg film used for the resistivity measurements in addition to the QCM sensor. The quartz substrate has four predeposited Au electrodes constituting the four-point probe arrangement. The resistivity was measured on a sample whose length = 10 mm, width = 1 mm. Sample thickness was typically 380 nm, except for the samples used in the high concentration runs where it was halved. A current of 2 mA was used for the resistance measurements, with a maximum power of 0.3 mW dissipated in the film at the highest resistivities.

The Pd layer deposited on top of the Mg film was

7 nm, which constituted a negligible addition to the Mg film conductivity (<0.8%), except when the resistivity of the Mg film becomes very high. The latter case arose during measurements of the resistivity changes at high hydrogen concentrations. The conductivity in Figs. 4 and 5 is indeed close to being restricted by the Pd contribution. All hydriding-decomposition cycles were performed in the high pressure cell at 0.6 torr and 350 K.

The cleanliness of the deposited Mg and Pd films was routinely checked by AES. Typical contamination levels were 5–7 at.% for the Mg film and 2 at.% for the Pd film. The surface topography of the freshly prepared samples and of the samples after a few hydriding-decomposition cycles was investigated by stylus profilometry and by scanning tunneling microscopy (STM). One hydrided sample was also investigated by ^{15}N depth profiling [4], to ascertain that H gradients perpendicular to the surface were weak, which indeed was the case.

3. Results and discussion

3.1. Low hydrogen concentrations, $H/\text{Mg} \leq 0.4$

Fig. 1 shows typical results obtained in the experiments used to determine the $\rho(x)$ vs. x relation ($x =$

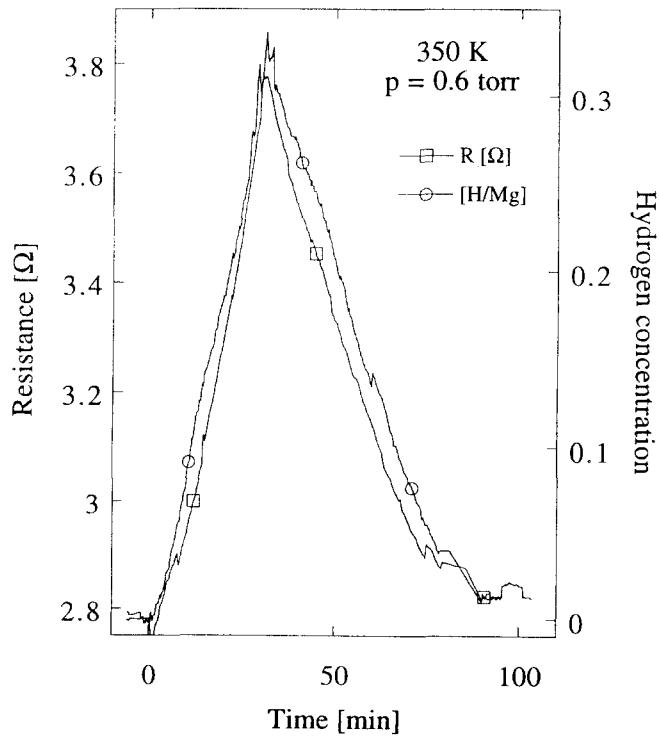


Fig. 1. Typical time evolution of the resistance and hydrogen concentration in the sample exposed to a hydrogen pressure of 0.6 torr at 350 K.

(H/Mg), atomic ratio). As H_2 is introduced in the high pressure cell ($p = 0.6$ torr, $T = 350$ K), both the H concentration in the sample and $\rho(x)$ increase nearly linearly with time, indicating a linear $\rho(x)$ vs. x relationship. At $(H/Mg) \leq 0.4$ the reaction cell is evacuated, and H_2 desorbs from the sample, with an accompanying decrease in resistivity, until all the hydrogen has desorbed.

In Fig. 2 the data of Fig. 1 are plotted as $\rho(x)$ vs. x (black dots). The shaded area in Fig. 2 shows a compilation of all the measured data (but excluding some data where obviously large cracks or loss of good electrical contact gave anomalous results). Fig. 2 illustrates data spread from sample to sample, and from run to run for each sample. Analyzing all our data we find, within experimental uncertainty, a strictly linear relationship of the resistivity vs. H concentration,

$$\rho(x) = \rho(0)(1 + c \cdot x),$$

where $c = 1.08 \pm 0.25$, which holds up to $x = 0.4$.

There was usually some hysteresis between the adsorption and the decomposition curves, and a small (few per cent) irreversible increase in the $\rho(0)$ resistivity after each hydriding cycle. A typical example of

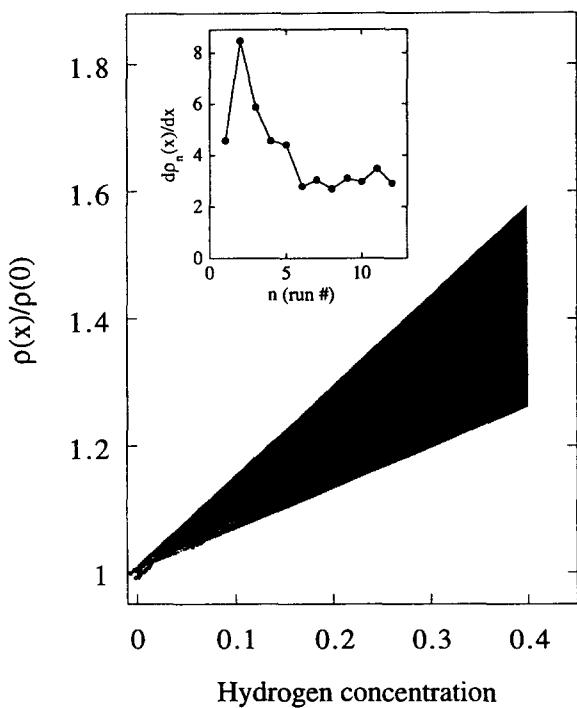


Fig. 2. Resistivity vs. uptake plot of the data from Fig. 1 (dots). The collected experimental data spread from a total of 28 hydriding-decomposition cycles performed on 8 different samples falls within the gray region. The inset illustrates the dependence of the incremental resistivity per absorbed at.% H on the cycle number, n . Similar dependence was observed for all samples used.

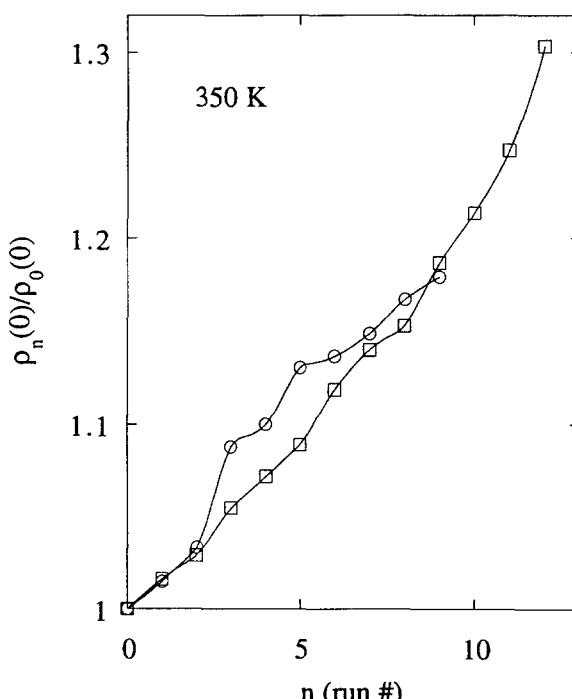


Fig. 3. The increase of the starting resistivity value with the number of hydriding-decomposition cycles.

this behaviour is shown in Fig. 3, where the ratio $\rho_n(0)/\rho_0(0)$ is plotted vs. n , where n denotes here the number of hydriding-decomposition cycles that the sample has been subjected to. We attribute these changes to the morphological changes that occur during hydriding-decomposition due to volume expansion-contraction. They include lattice defects, changes in grain size and micro cracks in the sample.

Another manifestation of morphological changes due to the hydrogen loading of the sample is seen in the inset of Fig. 2. It shows how $d\rho_n(x)/dx$, i.e. the resistivity change per at.% of hydrogen absorbed, varies with the number of absorption cycles, n .

As pointed out in the introduction, these changes reflect hydrogen-induced embrittlement of the sample, which affects both the resistivity measurements and the concentration measurements.

3.2. High hydrogen concentrations

At very high hydrogen concentrations the morphological changes (internal defects and cracks, etc.) of the sample films become increasingly severe. Again, this affects the $\rho(x)$ measurements as well as the mass uptake measurements. Since the two measurements are performed on separate sample films, one on the QCM crystal and one on the quartz substrate, these morphological changes are uncorrelated. They are both driven by the hydrogen content and by the accompanying volume expansion-contraction, but

their exact occurrences and other details may be different in the two samples. This introduces additional spread when $\rho(x)$ (measured on one sample) is plotted vs. x (measured on a different sample). For these reasons and because the morphological changes have a strong influence on the measured $\rho(x)$, we only emphasize the semiquantitative aspects of the high concentration data presented below.

Fig. 4 shows three successive runs with one sample, displaying $\rho(x)$ vs. x during hydriding (arrows pointing upwards) and decomposition. Also shown is the $\rho(x)$ vs. x curve from the hydriding cycle, obtained by using the volumetric rather than the QCM uptake method (dashed curve). The general behavior obtained with the two methods is the same, although there are substantial quantitative differences. This lack of quantitative agreement is partly related to the errors in the QCM reading at high x (due to e.g. influence of stresses in the sample film), and partly stems from the experimental artifacts during volumetric measurements (since the cell volume is small, even small gas leaks to the outside influence the pressure readings substantially).

Initially, with the hydrogen-depleted sample, the resistivity increase vs. x is weak and linear, as discussed above. For $x > 0.4$ the variation of $\rho(x)$ with hydrogen concentration becomes stronger than linear, but remains still rather weak until x reaches values

around 1–1.5. There the resistivity increases very rapidly by about a factor of 5. When the pressure cell is evacuated the H content decreases rapidly (see Fig. 5, which shows the raw data of uptake and resistivity, respectively, vs. time corresponding to the experimental data shown in Fig. 4). The resistivity does not follow the same trace upon dehydriding as during hydriding, but lies at much larger ρ values in the former case.

Our qualitative interpretation of these data is the following. During the hydriding cycle the hydride phase nucleates and grows as isolated grains in the continuous (metallic) α -phase and the conductivity is still kept high. When the hydride nuclei start to coalesce, there is a rapid reduction in high conductivity paths due to bottlenecks in the continuous, metallic phase, and the resistivity rises rapidly. The system is now approaching a continuous and insulating (or at least low conductivity) hydride phase, with isolated metallic phase grains. When at this point the hydrogen gas is evacuated, H_2 desorbs rapidly. The hydride phase is however still maintained as the continuous phase but with successively decreasing H content, keeping the resistivity of the sample at a high value. This creates a hysteresis in $\rho(x)$ vs. x for uptake and decomposition, respectively, corresponding to the plateau hysteresis usually observed in metal hydrides.

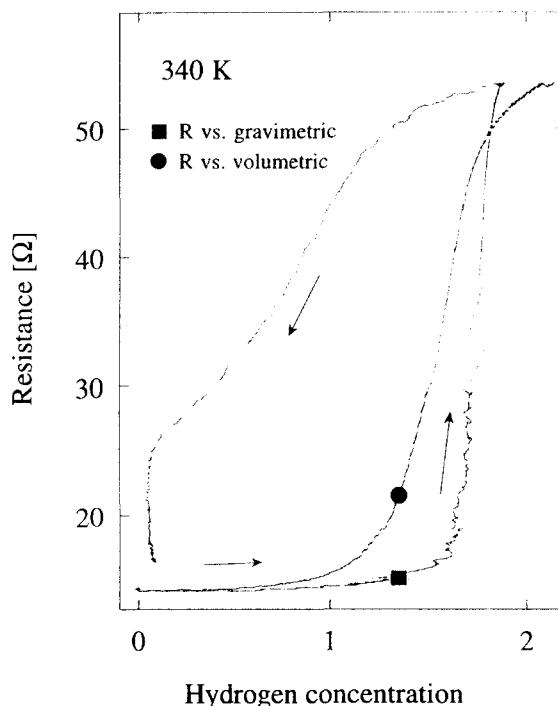


Fig. 4. Typical resistivity changes with hydrogen concentration in the experiments on 190 nm thick Mg films. The experimentally determined volumetric hydrogen uptake was calculated assuming that the volume of the hydriding cell was ≈ 100 ml.

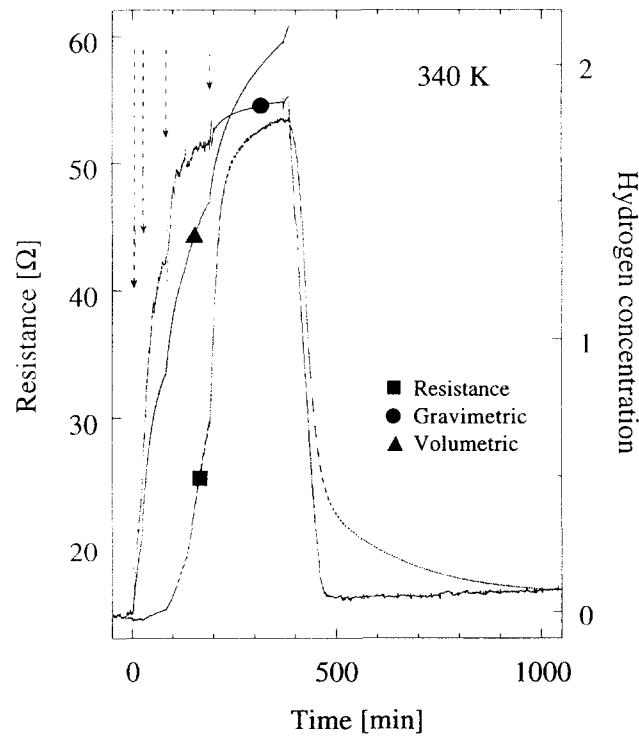


Fig. 5. Time evolution of the resistance and hydrogen concentration for the data presented in Fig. 4. The dashed lines indicate successive pressure increases (from left to right): 0.6 torr, 1.5 torr, 3.5 torr and 7 torr.

Only at quite low values of hydrogen concentration does the system transform back to a continuous metallic phase. When this happens the resistivity drops back, to nearly the initial starting value. The fact that the initial value is not totally recovered is attributed to the same type of irreversible morphological changes as discussed in connection with the $\rho(x)$ vs. x data for $x < 0.4$.

To summarize we have observed a nearly reversible linear behavior relation between $\rho(x)$ and x at $x = (\text{H}/\text{Mg})$ up to around 0.4. Hydriding to larger values in the range 1–1.5 reveals a rapid resistivity increase attributed to the beginning of a complete metal–insulator transition in the MgH_x system. This transition does not reverse until much lower x values than are reached during hydriding. The measurements and the interpretation of the data are influenced by morphological changes affecting both the $\rho(x)$ and x measurements, which inhibit a more detailed and quantitative analysis.

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