



Substrate effects on formation and hydrogenation of Mg–Ni films

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ABSTRACT

Usually metallic films for metal hydrides research applications are deposited on hard and flat substrates such as silicon, magnesium oxide, fused silica or quartz glass. With the film thickness increases all films during hydrogenation deals with typical problems such as film brittleness and cracking. In this paper we demonstrate that metal Mg–Ni films for hydrogen storage can be successfully deposited on to the flexible low surface energy expanded PTFE substrates. The received results for soft substrates (expanded PTFE) are compared to films being deposited on crystalline silicon substrate with and without plasma pretreatment. It is observed that different interface zone between substrate and film has great affect on both film crystallinity and its reaction with hydrogen. It is also demonstrated that modifying surface of the substrate might have affect on film microstructure before and after hydrogenation.

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1. Introduction

Metal hydrides were discovered in the beginning of the nineteenth-century but for a long time remained interesting only for the fundamental research [1]. However, the development of fundamental understanding and experimental observations of the metal hydride properties revealed their relevance to the industrial applications. For the last decades a lot of the research was focused to use metal hydrides in energy related applications [2–6]. It was shown that advanced solid state hydrogen storage systems potentially can become one of the key elements for the future energy systems, meanwhile rechargeable nickel–metal hydride batteries are already widely spread in the global market and successfully competes with the Li based alternatives [7].

Applications of thin films in metal hydrides research studies have gained separate interest because most of the Physical Vapour Deposition (PVD) technologies allow synthesizing nanostructured materials in much more controllable way in comparison to the chemical methods or semi-mechanical ball milling technique [8]. Furthermore, synthesis of the metallic films and its subsequent hydrogenation opened up possibilities for the in situ and

ex situ optical spectroscopy and electrical resistivity measurements which are difficult or even impossible to implement for the ball milled powders [9,10]. Indeed, then Huiberts et al. synthesized and hydrided yttrium and lanthanum films they observed that transition from dihydride to trihydride leads to the significant changes in optical and electrical properties of the films [11]. The later transition from the conductive metallic mirror state to transparent semiconductor or dielectric hydride phase was also observed for other metal hydrides including magnesium–rare-earth and magnesium–transition-metal hydrides [12–15]. These observations were important not only from the fundamental point of view but also opened up new areas for the metal hydride film applications such as hydrogen sensors and switchable mirror devices [16–20].

Mg₂NiH₄ hydride has theoretical hydrogen content of 3.6 wt.%, good hydrogen absorption–desorption cycle stability [21,22], moderate decomposition temperature [23,24] and exhibits optical switching phenomena then produced in thin film form [14,17]. Therefore it was a target of a lot of research both in hydrogen storage and metal-hydride-based devices (hydrogen sensors, switchable mirrors and recently even as possible candidate to replace silicon in solar cells) [25]. Mg₂NiH₄ has three crystal phases. Low temperature phases (below 510K) LT-1 and LT-2 both have monoclinic structure respectively without and with microtwinnings; and high temperature (HT) phase has FCC structure [26,27]. Blomqvist and Noréus demonstrated that at room temperature Mg₂NiH₄ powders of LT-1 phase has brownish-gray color meanwhile LT-2 phase powders has characteristic orange color [28].

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When heating across the LT → HT transition at 510 K, both phases transform to HT phase and change their color to black. Coiling down of HT phase Mg_2NiH_4 powders leads to the transition to LT-2 phase and reappearance of orange color independent of what phase powders were before heating up. At the same article authors demonstrate that both conductivity and crystal structure of Mg_2NiH_4 powders is affected by the applied mechanical stress [28].

All these features of Mg_2NiH_4 hydride and particularly its phase changes resulting into different conductivity and optical properties boosted research for Mg_2NiH_4 synthesis in thin film form. It was expected that hydrogenation properties of Mg_2Ni alloy thin films will be similar to powders, whereas experiments showed that situation with thin films is more complicated. Contrary to expectation our earlier study has shown that hydrogenation of Mg_2Ni films formed on quartz and calcium fluorite substrates results into pseudo cubic phase (instead of LT-1 for hydrogenation temperatures below 510 K) which remains unchanged over all temperature range from room temperature up to its decomposition at around 550 K [29,30]. Gremaud et al. investigated optical properties of $\text{Mg}_y\text{Ni}_{1-y}\text{H}_x$ gradient thin films which were hydrided at room temperature and also reported yellow-to-red colors suggest that it could have been LT-2 or pseudo cubic phase (experimentally measured hydride structure was not reported) [31]. But Jain et al. showed that formation of crystalline monoclinic Mg_2NiH_4 phase is also possible [32] whereas Westerwaal et al. claimed that in film form Mg_2NiH_4 hydride is amorphous [33,34]. Interestingly, later group has demonstrated that hydrogenation of Mg_2Ni alloy starts by formation of α hydride phase ($\text{Mg}_2\text{NiH}_{0.3}$ solid solution) at the interface with the substrate followed by the β hydride phase which also forms at the interface and proceeds to the film surface [33].

Up to the best of our knowledge there were no systematic approaches to investigate what factors introduced by magnetron sputtering technique or thin film interaction with substrate are responsible for the dissimilarities between Mg_2NiH_4 hydride properties in film and powder forms. However, it is highly believable that it is substrate and its interaction with the thin film that becomes the main factor affecting hydrogenation properties. Experimental observations indicate that when hydrogen enters the film the in-plane expansion is limited and this introduces the in-plane stress which changes the thermodynamic properties compared to the corresponding bulk material [35,36]. Another group demonstrated that hydrogenation of Mg thin films deposited on porous and non-porous substrates can have effect for the micro-strains inside the film which alters Mg film hydrogenation properties [37]. Considering later information in this work we wanted to test if using dissimilar substrates and varying their pretreatment conditions we could have significant effects on hydrogenation properties of Mg_2Ni films deposited by magnetron sputtering.

2. Materials and methods

In this work we used PVD-75 magnetron sputtering system manufactured by Kurt J. Lesker company with two independent 3" size Torus DC powered magnetrons. The system was equipped with cryopump which allows to achieve a base vacuum level down to 5×10^{-8} mbar (5.05×10^{-6} Pa). For sputtering we used 99.99% purity magnesium and 99.999% purity nickel targets obtained from Kurt J. Lesker Company. As it was already mentioned during our earlier experiments [29] as substrates we have used amorphous quartz and polycrystalline calcium fluorite. Therefore, in order to check if usage of different substrates have effects on Mg_2NiH_4 hydride formation properties we have chosen two types of substrate with completely opposing properties from those which were used

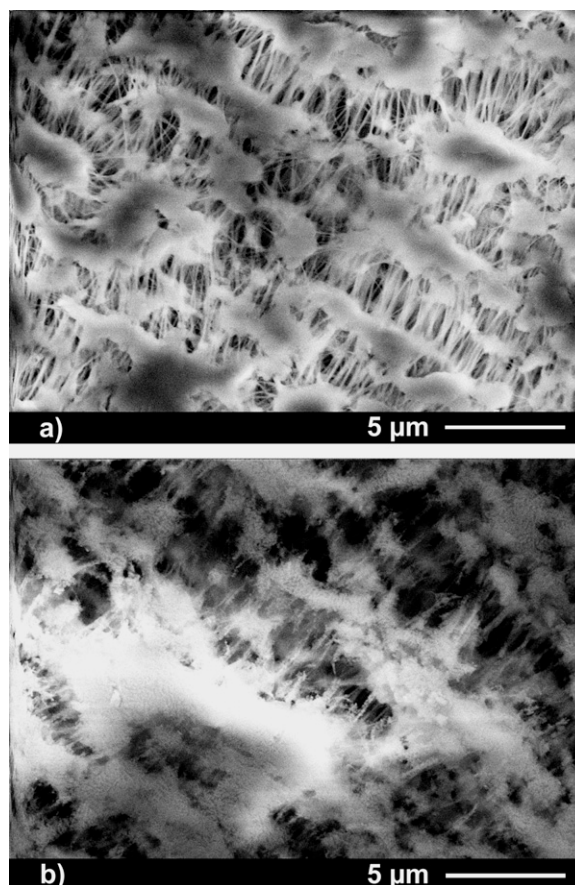


Fig. 1. SEM images of expanded PTFE substrates: (a) expanded PTFE substrate washed with acetone/alcohol and (b) expanded PTFE substrate was washed with acetone/alcohol and treated with pulsed DC plasma.

during earlier experiments. First of them was polished prime grade silicon wafers with (1 1 1) surface orientation received from Siebert Consulting e.K. In contrast to quartz and CaF_2 , silicon wafers have flat and periodical surface even at the atomic scale which is guaranteed by (1 1 1) crystalline orientation. Furthermore, it is known that at higher temperatures (around 600 °C) magnesium and silicon can form magnesium silicates [38] which can suppose much higher Mg–Ni film and substrate interaction comparing to film–substrate pairs used in earlier studies. For the second substrate we were looking for substrate with as low surface energy as possible. We have chosen to use expanded PTFE from W.L. Gore & Associates Inc. Expanded PTFE is widely known for very low free surface energy and apart from that it also (i) exhibits very good temperature stability in -268 °C to $+315$ °C temperature range; (ii) is dimensionally stable with no aging or degradation; (iii) chemically inert-resistant to all media in the 0–14 pH range, except molten alkali metals and element fluorine; (iv) possible operating pressure from vacuum up to 200 bar. The combination of low surface energy, chemical inertness of the expanded PTFE substrate as well as its flexible microstructure is expected to result in much smaller micro-strains which are formed in Mg–Ni–H films.

For both types of substrates we have used three different surface pre-treatment procedures. For the first group of samples Si and expanded PTFE substrates were washed in acetone in ultrasonic bath, dried out under dry air flow and then wiped out with cloth rinsed in ethyl alcohol. Substrates for the second group of samples in addition to washing as described above before film deposition were affected by DC power source generated plasma (no contact with air between plasma treatment and thin film

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