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Review article

Hydrogen storage characteristics of Ti– and V–based thin films

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ABSTRACT

Series of thin films of single-, bi- and tri-layered structure consisting of Ti, V, TiO_2 and V_2O_5 layer and/or mixed Ti–V–Ni layer with different layer sequences and thicknesses were prepared by the sputtering technique on Si and SiO_2 substrates. The layer chemical composition and thickness were determined by a combined analysis of X-ray diffraction, X-ray reflectometry, Rutherford backscattering and optical reflectivity spectra. The films were hydrogenated at 1 bar at 300 °C and/or at high pressures up to 100 bar at room temperature. The hydrogen concentration and hydrogen profile was determined by means of a secondary ion mass spectroscopy and N-15 Nuclear Reaction Analysis. The highest hydrogen storage with a concentration up to 50 at.% was found in the pure Ti layers, while it amounts to about 30 at.% in the metallic Ti–V–Ni layers. A large hydrogen storage (up to 20 at.%) was also found in the V_2O_5 layers, while no hydrogen accumulation was found in the TiO_2 layers. Hydrogen could remove the preferential orientation of the Ti films and induce a complete transition of V_2O_5 to VO_2.

1. Introduction

Hydrogen and fuel cells are considered as key solutions for the 21st century, offering a clean and efficient production of power and heat especially without any negative impact on environment. Hydrogen storage is thus becoming a materials science challenge in developing hydrogen economy. One of the main goals is to search for optimal hydrogen-storage materials which could have higher volume densities than pressurized and/or liquid hydrogen. Besides, a very important criterion for a hydrogen storage system is the reversibility of hydrogen uptake and release [1,2].

Metals, intermetallic compounds and alloys generally react with hydrogen and form mainly solid metal-hydrogen compounds. They can absorb a large amount of hydrogen and release it easily again upon heating. They are predominantly metallic in character and thus referred to as metallic hydrides (or metal hydrides). Such systems with reversible hydrogen reaction are potential hydrogen storage media. Beside of volume-efficient storage, the advantage of metal hydrides is that they are stable and can be maintained at room temperature (while e.g. the liquid hydrogen has to be maintained at low temperature $T = 20$ K).

The most widely utilized metal hydrides are MgH_2 and $LaNi_5H_6$. MgH_2 has a high storage capacities of hydrogen as much as 110 kg-H_2/m^3 (=6.5H atoms/cm^3 (x10^{22})). The volumetric hydrogen density of $LaNi_5H_6$ is similar (115 kg-H_2/m^3). They are much higher than that of liquid hydrogen (70.85 kg-H_2/m^3 (=4.2 H atoms/cm^3 (x10^{22}) below 20 K) and hydrogen gas (0.09 kg-H_2/m^3 (=0.99 H atoms/cm^3 (x10^{22}) at 200 bar). MgH_2 is considered to have a highest gravimetric density of 7.6 wt% H. (The gravimetric density of $LaNi_5H_6$ is of 1.3 wt% H). Besides, MgH_2 has the highest energy density (9 MJ/kg Mg) of all reversible hydrides applicable for hydrogen storage [3–5]. We notice here that different references give the H-storage in different units. For the sake of comparison, we include cited data in all commonly used units for the bulk samples.

From the fundamental viewpoint, the search for hydrogen storage materials brings up the important issues for research. Introduction hydrogen (with a very small atomic size) into the crystal lattice indeed brings a small perturbation to the system (e.g. a lattice expansion, a modification of the crystal and electronic structure and the hydrogen bonding with other atoms in the lattice). The new-formed hydrides, however, often exhibit new and fascinating physical properties. Thus, it is necessary to understand the mechanism involved in the interaction of hydrogen with matter in the solid-state form and to investigate the (new) properties of the hydrides. Another important issue is that the reduction of the particle size to the nanometer range results in an enhancement of

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kinetics of hydriding and dehydriding. Besides, nanostructure forms often display modified behavior compared to the bulk. Thus the new tendency of research nowadays is to concentrate on nanomaterials for hydrogen storage [6]. For instance, faster hydrogen sorption rates were found for the nanocrystalline Mg_2Ni than that of their bulk counterpart due to an enhanced surface effect and a shortened diffusion path [7]. A reduction of the grain size in MgH_2 can also decrease the reversible storage capacity related to a reduction of intragrain volume [8] as well as alter the stability due to a decrease of desorption energy [9]. Extended investigations have been focused on carbon nanotubes (CNTs) [10–12], TiO_2 nanotube composites [13] as well as combined CNTs and TiO2 nanotubes [14], since they are promising candidates for reversible H_2 storage under normal conditions of temperature and pressure.

We are interested in the hydrogen storage capacity in Ti- and V-based thin films including their oxides and the effect of hydrogen sorption on their crystal and electronic structure and physical properties. We remind here that thin film processing is an alternative method for synthesizing nanostructured materials (which could provide a size-reduction to the nanoscale). We have prepared and investigated numerous thin films with different layer structures, sequences and layer thicknesses: 1) the Ti– and TiO_2–based thin films, 2) the TiO_2– and V_2O_5–based thin films and 3) the Ti-V films with Ni doping. We have investigated the films in different states: 1) in the as-deposited state and 2) after hydrogenation. We tend to understand the role of the atom mixing and diffusion across the film interfaces, the precipitation of nanoparticles on the hydrogen absorption rate as well as the reversible effect of the hydrogenation on the thermodynamic properties of the films. In particular we focus on the possibility of hydrogen storage in these films under different conditions. Details of our investigations of those mentioned-above thin film systems have been reported elsewhere [15–19]. In this paper, we review the most important outcome of our research.

2. Experimental

Thin films consisted of Ti, TiO_2 and V_2O_5 with different layer geometry, sequences and layer-thicknesses and the mixed Ti–V–Ni layers have been deposited by means of magnetron *dc* pulse sputtering system on Si(111) and silica SiO_2 substrates. Prior and during deposition the substrates were heated up to 250 °C. The total film thickness was in the range of 40–200 nm. The high purity Ti/V target (4N) was sputtered either in high purity argon (for pure Ti and V layer deposition) or in controlled Ar + O_2 reactive gas atmosphere (for TiO_2 and V_2O_5 layer deposition). For Ti-V and Ti–V–Ni thin film deposition, Vanadium and Nickel plates were placed on Titanium target to obtain Ti:V:Ni ratio of 1:1:1 and 0.6:0.1:0.3 respectively.

The hydrogenation experiments have been carried out for chose film series, either at atmospheric pressure (1 bar) and at 300 °C [16] or at high hydrogen pressures up to 100 bar and at room temperature [17]. One series of films was covered by an additional Pd layer (Pd caping) for possible improving of hydrogen storage characteristics of the films.

The layer chemical composition and layer thickness after depositions were determined by a combined analysis of X-ray diffraction (XRD), X-ray reflectometry (XRR), Rutherford backscattering (RBS) and optical spectrometry. RBS and XRR experiments have been performed on films before and after each hydrogenation to underline the changes of the film composition and structure upon hydrogenation. Details of XRR and RBS data analysis, especially the estimate of composition and layer-thickness, have been reported in [15,19].

The hydrogen quantity in the thin film systems is very small to be qualified by desorption. Thus we used a secondary ion mass spectroscopy (SIMS) and Nuclear Reaction Analysis using the ^{15}N beam (^{15}N-NRA method with $^{1}H(^{15}N, \alpha,\gamma)^{12}C$ reaction) for determination of hydrogen concentration in the films [18,19]. Besides, unlike the bulk samples, for the thin film systems as in our case with very thin layers, it is convenient to use the atomic percent for the very small amount of hydrogen.

3. Hydrogen storage up to 50 at.% in the Ti layers

Titanium and its alloys have a high affinity for hydrogen at elevate temperatures [20,21]. Hydride precipitation in Ti increases largely with increasing temperatures: it can pick up more than 50% at. H at elevate temperatures above 600 °C [22]. Thus they are considered as promising materials for hydrogen storage applications. Besides, the hardness of Ti hydride was found to be about 30% higher than that of pure Ti [23].

Since the discovery of water splitting into hydrogen and oxygen on TiO_2 electrodes in a photoelectrochemical (PEC) cell [24], titanium dioxide has become the most studied among photocatalytic materials presented in thousands published papers including many reviews and monographs [25–27]. Recently, the research has been performed on off-stoichiometric $TiO_{2\text{-x}}$, or anion- and cation-doped TiO_2 [28,29] in the search of modifying properties to increase its energy conversion efficiency [30,31]. Extensive investigations have been also focused on development of TiO_2 nanostructure forms or the Ti–TiO_2 systems for renewable energy sources and hydrogen economy (as mentioned above [11–13]). Thus, understanding the structural and thermodynamical properties of Ti–TiO_2 system as well as their hydrogen absorption ability is critical for the successful implementation of these materials. Although it is known that diffusion of hydrogen in TiO_2 is slower than that in the pure metal, the mechanism by which the oxide influences hydrogen permeation into Ti and its alloys is still not well established.

We aim at characterization of the film structure and properties of the Ti–TiO_2 thin film systems, in particular the influence of hydrogen intake on the microstructure and electronic structure of the films and the hydrogen storage ability in these systems [15–17]. The main outcome of our investigated were summarised as follow:

- For the Ti/TiO_2/Ti/Si(111) film (with the layer thickness of each layer in the range of 40–100 nm), hydrogen charging at 1 bar for 3 h leads to an accumulation of hydrogen in the top Ti layer (surface layer) up to 40 at.%.
- With 20 nm-thick layer of Pd caping (Pd/Ti/TiO_2/Ti/Si(111) film), the accumulation of hydrogen in the top titanium layer is enhanced (up to 50 at.%). The crucial point is that the hydrogen accumulation in the bottom Ti layer (deposited on the Si substrate) was increased from 15 at.% (i.e. without Pd caping) up to almost 50 at.% (with Pd caping). It indicates that Palladium is such a good catalyst also in this case. It is well known that Pd helps to dissociate the H_2 molecules which promotes hydrogen penetration resulting in a large enhancement of the hydrogen storage in the Ti films.
- No hydrogen storage was found in the TiO_2 layers indicating that hydrogen diffuses through the TiO_2 layer without any accumulation there, both for the films with and without Pd caping. Due to the columnar-structure of TiO_2 layers, larger open channels for hydrogen diffusion are found to parallel to the *c*-axis and thus the hydrogen diffusion through a TiO_2 can be faster in this direction [32]. We remind here that no significant hydrogen storage capacity was found in nanotubular TiO_2 arrays [13], while TiO_2 nanotubes can reproducibly store up to ~2 wt% H_2 at room temperature but under a high pressure of 6 MPa [11].