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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, TiO₂ and V₂O₅ layer and/or mixed Ti–V–Ni layer with different layer sequences and thicknesses were prepared by the sputtering technique on Si and SiO₂ 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 V₂O₅ layers, while no hydrogen accumulation was found in the TiO₂ layers. Hydrogen could remove the preferential orientation of the Ti films and induce a complete transition of V₂O₅ to VO₂.

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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 MgH₂ and LaNi₅H₆. MgH₂ has a high storage capacities of hydrogen as much as 110 kg-H₂/m³ (=6.5H atoms/cm³ ($\times 10^{22}$)). The volumetric hydrogen density of LaNi₅H₆ is similar (115 kg-H₂/m³). They are much higher than that of liquid hydrogen (70.85 kg-H₂/m³ (=4.2 H atoms/cm³ ($\times 10^{22}$)) below 20 K) and hydrogen gas (0.09 kg-H₂/m³ (=0.99 H atoms/cm³ ($\times 10^{22}$)) at 200 bar). MgH₂ is considered to have a highest gravimetric density of 7.6 wt% H. (The gravimetric density of LaNi₅H₆ is of 1.3 wt% H). Besides, MgH₂ 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 TiO_2 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 those 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 capping) 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 $^1H(^{15}N, \alpha, \gamma)^{12}C$ 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-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 capping (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 capping) up to almost 50 at.% (with Pd capping). 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 capping. 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].

- Upon applying a high pressure of hydrogen up to 100 bar, a large hydrogen storage in the thick Ti film (with the layer-thickness > 240 nm) was obtained. It implies a large film-swelling.

As a summary, we show in Fig. 1 the hydrogen profile determined by ^{15}N -NRA for the Ti/TiO₂/Ti/Si(111) films revealing the large hydrogen storage up to 40–50 at.% and the role of Pd as a catalyst for hydrogen absorption. Unfortunately, after the ^{15}N -NRA experiments, the layers were easily peeling off and thus we could not perform the RBS experiments for the films after hydrogenation. More detail interpretation of our results can be found in our previous publications [16,17].

4. Hydrogen storage in V₂O₅ films and the V₂O₅–VO₂ transition assisted by hydrogen

Vanadium dioxide (VO₂) has been mostly known for its metal-insulator phase transition at a technologically useful temperature T_{MIT} of 340 K (67 °C). Vanadium pent-oxide (V₂O₅) has been considered as materials for electrochromic and electrochemical devices and microbatteries [33,34]. A large interest is focusing on investigations of TiO₂–V₂O₅ thin films to gain the optimal electrochromic properties due to their potential applications for electrochromic smart windows and other electrochemical devices [35], e.g. the VO₂–TiO₂ multilayers have a higher luminous transmittance than that of a single VO₂ film and could yield a large change of solar transmittance at both temperatures below and above T_{MIT} of VO₂ [36].

We have carried out investigations of the TiO₂–V₂O₅ and V₂O₅–TiO₂ thin films (i.e. with different layer-sequence depositions) on SiO₂ substrates. The most important outcome of our investigations of the films after deposition (i.e. in the as-deposited state) is summarized as follow:

- If we start first with titanium oxide deposition and then continue with vanadium oxide deposition, we were not able to get a stoichiometric TiO₂ layer. Due to both V- and Si diffusion into TiO₂ layer, we got a mixed dioxide layer (MO₂ where M = Ti, V, Si) on the SiO₂ substrate. The vanadium oxide layer on the film surface, however, is always a stoichiometric V₂O₅ layer. For

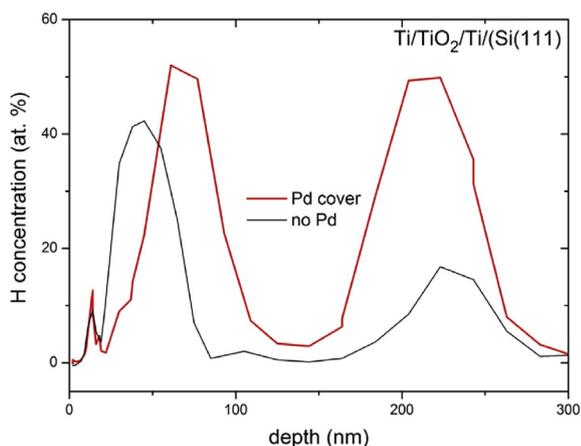


Fig. 1. Hydrogen profiles determined by ^{15}N -NRA for the Ti/TiO₂/Ti/Si(111) film without Pd covering and with Pd covering revealing a large hydrogen storage up to 50 at.% in the Ti layers, while hydrogen was not accumulated in TiO₂ layer. Pd layer plays a good role of catalysis to enhance the hydrogen storage in the deep Ti layer.

a simplicity, we still use the notation as the nominal composition V₂O₅/TiO₂/SiO₂ (instead of a correct composition of V₂O₅/MO₂/SiO₂).

- We could obtain both stoichiometric V₂O₅ and TiO₂ layers (on the film surface) in the case when we deposited the vanadium oxide first and then the titanium oxide layer, i.e. TiO₂/V₂O₅/SiO₂ film. In this case no Si or Ti inter-diffusion into V₂O₅ layer was detected (within e.g. the RBS error limit). In other words, a sharp borderline at V₂O₅ layer–SiO₂ substrate and at TiO₂–V₂O₅ layer was always obtained.

Most of films are charged by hydrogen twice (denoted as H(1) and H(2)) each with 3 h. As an example, we show in Fig. 2 (top) the N-15 results obtained for TiO₂/V₂O₅/SiO₂ film with a total film thickness of 184 nm. For a clearer demonstration of the hydrogenation effect, i.e. the change of the layer-thickness and chemical composition upon hydrogenation, we construct the film diagram (Fig. 2, bottom). The layer thicknesses are drawn proportionally with respect to the values estimated from the RBS but in cm-scale instead of nm-scale to guide the eyes. Different colors indicated different chemical composition in the layers. We summarize the

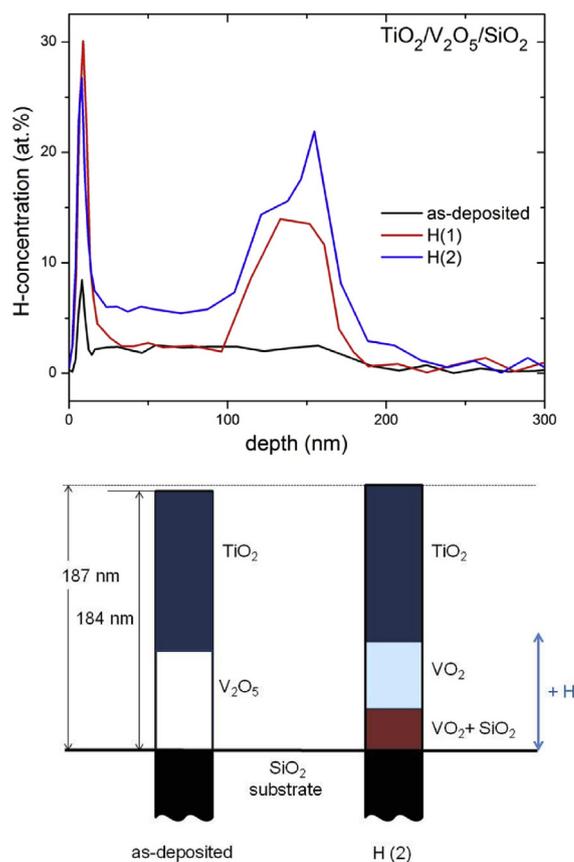


Fig. 2. Top: Hydrogen profiles determined by ^{15}N -NRA for TiO₂/V₂O₅/SiO₂ film after two hydrogen charging circles each for 3 h (H(1) and H(2)). A hydrogen storage of 20 at.% was found in the deep layer about 100 nm beneath the surface. Bottom: The film diagrams illustrated the influence of hydrogenation on the film structure and composition after total 6 h of hydrogen charging (H(2)). The solid black line indicates the original separation between the film and the SiO₂ substrate. The blue-colored perpendicular line indicated the hydrogen in the layer-thickness determined from N-15 experiments, i.e. in the V₂O₅–VO₂ layer. The layer thicknesses determined from RBS analysis are drawn proportionally with respect to the values estimated from the RBS, but in cm-scale (1 cm is equivalent to 20 nm) to guide the eyes. Different colors indicated different chemical composition in the layers.

obtained results on the $\text{TiO}_2/\text{V}_2\text{O}_5/\text{SiO}_2$ films upon hydrogenation as follow:

- hydrogen diffuses through the surface TiO_2 layer and does not accumulate there: a very low hydrogen content was found in the thickness range down to about 100 nm with respect to the film surface (i.e. the thickness of TiO_2 layer).
- Hydrogen reaches an average value of about 15–20 at.% at the depth of 100–180 nm, i.e. in the vanadium oxide layer.
- The total film thickness does not change much; it increases only by 2% of the original thickness.
- A very large reduction of V_2O_5 is observed under hydrogen charging. After 6 h, a complete transition of V_2O_5 into VO_2 was achieved.

A visible hydrogen effect on the film structure and properties was also observed for $\text{V}_2\text{O}_5/\text{TiO}_2/\text{SiO}_2$ film with a film thickness of 122 nm. In this case, a large increase of the total film thickness was up to 15% of its original value. Hydrogen charging leads to a large decrease of the TiO_2 portion and a large increase of the SiO_2 portion in the mixed MO_2 layer, as a consequence of a larger Si diffusion from the substrate.

For both films, the stoichiometric TiO_2 and/or V_2O_5 layer was well preserved upon the film surface: the layer thickness is almost unchanged upon hydrogen charging [19]. Thus the swelling effect seems to be related the mixed $\text{TiO}_2\text{--VO}_2\text{--SiO}_2$ layer (i.e. consisted of TiO_2), whereas the mixed $\text{VO}_2\text{--SiO}_2$ layer does not lead to a visible film swelling.

5. A large hydrogen storage (~30 at.%) in the metallic Ti–V–Ni layers

We extended our investigations of the hydrogen absorption capacity in thin film system consisted of Ti and V, such as Ti–V system with Ni-doping. For the film deposited on Si(111) substrate, the composition of the films determined from RBS experiments are 36 at.% Ti, 34 at.% V and 30 at.% Ni (marked as $\text{Ti}_{36}\text{V}_{34}\text{Ni}_{30}/\text{Si}(111)$), quite close to the nominal ratio (1:1:1). The film thickness is estimated to be 151 nm, i.e. equal to the nominal value. For the film deposited on SiO_2 substrate, the element composition was found to be in a good agreement to the nominal one: 55 at.% Ti, 10 at.% V and 35 at.% Ni ($\text{Ti}_{55}\text{V}_{10}\text{Ni}_{35}/\text{SiO}_2$). The film thickness is estimated to be 178 nm, i.e. larger than the nominal thickness [19].

Hydrogen profile determined from N-15 experiments and the film diagram for Ti–V–Ni/Si(111) film is presented in Fig. 3. Before hydrogen charging, Ti–V–Ni layer reveals a small amount of hydrogen (~4 at.%) distributed quite homogeneously within the whole film up to 100 nm deep from the film surface. On the surface (up to the thickness of 10–15 nm) a quite high concentration of 15 at.% of hydrogen is found. Hydrogen charging causes a large increase of hydrogen amount up to 32 at.% in the film. However, the hydrogen profile reveals that the hydrogen gathers mostly in the depth of the range of 50–100 nm, i.e. in the deep layer consisted of Ti, V and Ni metal (i.e. free of oxygen).

The hydrogen profile obtained by N-15 technique and the film diagram for Ti–V–Ni/ SiO_2 film is shown in Fig. 4. Similarly, before hydrogen charging an amount of hydrogen up to ~4 at.% is homogeneously distributed in the film. After hydrogen charging process, a significant increase of hydrogen concentration is revealed. Moreover, hydrogen was found to accumulate at the depth (from the film surface) of 100–200 nm, i.e. corresponding to the region consisted of high Ti, V and Ni content (>70 at.%). The hydrogen amount reaches 28 at.%, i.e. lower than that in the film deposited on Si(111) substrate.

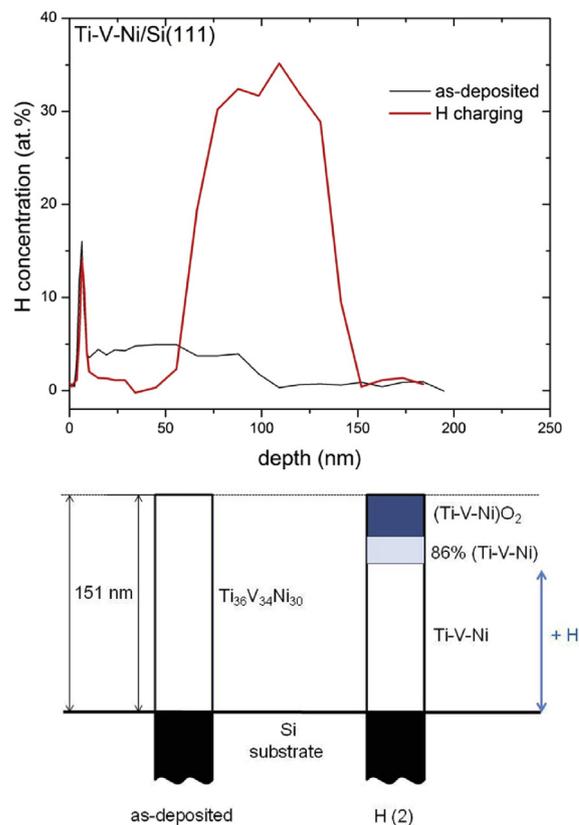


Fig. 3. Hydrogen profile determined by ^{15}N -NRA for Ti–V–Ni layer on Si(111) before (as-deposited) and after hydrogen charging (top) and the film diagram (bottom) determined from RBS analysis (see figure caption of Fig. 2). A large hydrogen storage (~32 at.%) was revealed in the deep layer of about 50 nm beneath the surface, i.e. in the metallic Ti–V–Ni layer.

For a more detail of estimated values for layer composition and thickness influenced by hydrogenation, see the table 1 and 2 in our recent publication [19]. We summarized our obtained results on Ti–V–Ni film series as follow:

- The film surface was oxidized upon hydrogen charging and it consists mostly TiO_2 . The results again confirm that hydrogen can diffuse through the oxide layer without gathering there.
- A large hydrogen storage (28–32 at.%) was found in the (alloying) layer consisted mostly of Ti, V and Ni metal. The hydrogen storage does not lead to any visible change of the layer thickness. It may indicate that the metal layers can have more interstitial sites for hydrogen and that hydrogen storage does not need any lattice expansion.
- The higher hydrogen storage is found in the film with a higher Ti content indicating that titanium seems to have a higher hydrogen absorption capacity (than vanadium).
- The large swelling effect is attributed to the TiO_2 : the layer consisted of a larger portion of TiO_2 always shows a larger thickness increase. This suggestion was supported by the observations on $\text{TiO}_2\text{--V}_2\text{O}_5$ film series: a larger swelling effect was found for the mixed $\text{TiO}_2\text{--VO}_2\text{--SiO}_2$ layer than that of $\text{VO}_2\text{--SiO}_2$ one.

By using metal (Si) and metal-oxide substrate (SiO_2), despite of different composition and layer thickness, we are able to show that the metallic (alloying) layer consisted of Ti, V and Ni can store the hydrogen.

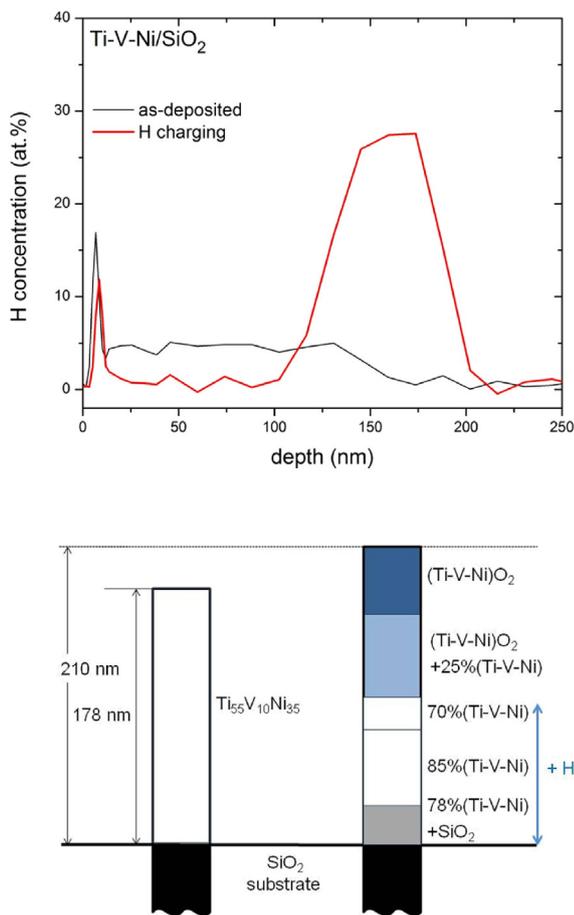


Fig. 4. Hydrogen profile determined by ^{15}N -NRA for Ti-V-Ni layer deposited on SiO_2 before (as-deposited) and after hydrogen charging (top) and the film diagram (bottom) determined from RBS analysis (see figure caption of Fig. 2). A quite high hydrogen storage rate (~ 28 at.%) was revealed in the deep layers consisted mostly Ti-V-Ni ($>75\%$).

6. Conclusions

The most important findings of our investigations on 3 different thin film systems consisted of Ti, V and their oxides are: 1) the largest hydrogen amount (with hydrogen content up to 50 at.%) can be stored in the Ti film or in the thin film systems consisted of pure Ti layer, 2) palladium could act as a good catalyst for hydrogen diffusion into the films and leads to a large enhancement of hydrogen storage, 3) hydrogen could be also stored in the V_2O_5 - VO_2 layer (~ 20 at.%) and/or in the metallic (alloying) layer consisted of Ti, V and Ni metal (~ 30 at.%). Besides, the introduction of hydrogen into the films could induce a V_2O_5 - VO_2 transition.

This research contributes to the study of hydrogen storage in Ti-V based thin films as well as the hydrogenation effect on their structure and physical properties. Our results indicate that those thin film systems could be a good candidates for hydrogen storage materials.

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