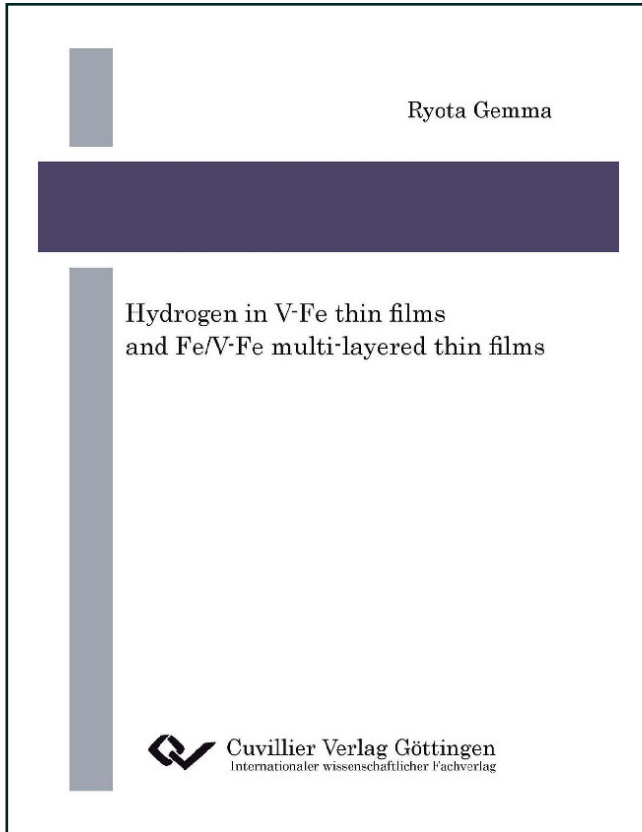




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Hydrogen in V-Fe thin films and Fe/V-Fe multi-layered thin films



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1. Introduction

Ever since the energy crisis in 1970's, hydrogen (H) has been regarded as one of the carbon-free secondary energy sources. In this context, hydrogen storage materials have been considered as possible candidates of clean energy storage media (see e.g. website of Department of Energy in US [DOE]). Hydrogen is the smallest and the lightest element and thus can be easily absorbed in interstitial sites of metal lattice. A pioneering work in this field is known by Sieverts [Siev29]. In some of metal alloys with tailored composition, considerable amount of hydrogen (several wt%) can be reversibly stored through metal/metal hydride (MH) phase transition, just by controlling pressure or temperature [Vught70]. Practically, some of them (LaNi₅, TiFe) are really easy to handle and have already been utilized for technical applications like in fuel cell system [Iwas03] or in MH refrigerator [Uchi04] after intensive studies and developments in this field. Owing to its extraordinary high volume density and high stability, such metal hydrides still hold advantage to other storage methods like liquid hydrogen or high-pressure H₂ gas tanks. Currently, further research and development is on the way focusing on improvement of gravimetric hydrogen density and reaction kinetics [Orimo07, Dornh07].

In relation to this, nano-structuring has been attracting attention since early 90's to improve total performance including thermodynamics of M-H reaction. In fact, many studies report that metallic nano-clusters and metallic thin films have rather different, as well very interesting hydriding reaction properties from that of massive metals. Such aspects are reviewed in detail by Pundt and Kirchheim [Pundt06]. This new aspect, therefore, calls revisit of fundamental physics on metal-hydrogen system. For this purpose, it is important to choose well-investigated metals like Pd or V, as their properties have been well investigated on bulk scale and thus the discussion can be carried out on robust knowledge.

Based on this, a detailed investigation of H-related behavior at hetero-interfaces of multi-layered thin films can be carried out. Thereby, the local chemistry at the interfaces is strongly modified and, thus stark contrast to bulk-behavior is expected.

Usually, in massive metals, hydrogen absorption in interstitial sites induces lattice expansion in three dimensions. This process rather enables formation of cracks at the surface, through dislocation nucleation, which finally supplies fresh surface for hydrogen to be introduced in the metal or alloy easily.

In case of a metallic thin film, however, the film is deposited usually on elastically hard substrate. As long as the film is fixed to the substrate,

free volume expansion of the film is not allowed and the lattice expands one dimensionally in the film's out-of-plane direction by Poisson response (linear elasticity theory e.g. in [Slaug02]). Consequently, the stress field in the film's in-plane directions becomes highly compressive. Such anisotropy of stress field would induce anisotropic displacement of lattice in x,y and z directions and, thus causes directional dependence of H-H interaction in the film. Such mechanical boundary conditions are suggested to change thermodynamics of MH reaction [Alefeld72]. That is, even the initial displacement (stress) of the lattice in the film modifies the interaction in the same way.

By constituting a multi-layered film, it is possible to tune this initial stress state. In a Fe/V multi-layered epitaxial film, for example, the V lattice as the H absorbing layer feels in-plane compressive stress due to the adjacent Fe layers because lattice constant of Fe is smaller than that of V. Thus the out-of-plane V lattice is expanded already at as-deposited state. In combination of Mo/V, inverse situation can be established, as Mo has larger lattice constant than that of V. Primarily, the H-absorption behavior in V is very sensitive to such lattice strain and, accordingly, hydrogen absorption site is drastically changed [Koike81]. Constitution of the Fe/V strained-multi-layered film would establish anisotropic strain distribution since each V layer is both chemically and mechanically isolated by the adjacent Fe layers. This situation in turn modifies elastic boundary condition. Interestingly, this modification strongly influences different aspects of H-related phenomena.

The group of Hjörvarsson has intensively studied the thermodynamics of the above mentioned Fe/V and Mo/V superlattice systems with (100) orientation on hydrogen absorption for many years. For a review article, see e.g. Ref. [Hjörv97]. They have successfully demonstrated that stronger attractive H-H interaction is present in in-plane direction of Fe/V than that of V, while it is repulsive in out-of-plane direction, which is closely linked with gigantic out-of-plane expansion at low concentrations observed by XRD [Hjörv97]. These observations were finally discussed in terms of site occupation. They concluded that preferential O_z site occupation occurs in tetragonally distorted V lattice of Fe/V system throughout the whole concentration range (< 0.5 H/V). This situation was regarded as polarized elastic dipole formation [Alefeld72, Ander97]. Such particular case cannot be described by the above mentioned linear elasticity theory and remarkable departure from in-plane compressive stress development behavior is expected.

It is also worth to note that they did not observe any trace of hydride formation for the films with 2 nm V layer thickness. Usually, when the

hydrogen concentration exceeds the solubility limit, misfit dislocations are formed in the film. Miceli *et al.* have reported misfit dislocation formation in Nb/Ta epitaxial films by XRD measurement of H-loaded sample [Miceli91]. In extremely reduced dimension, incoherent phase transition may be hindered due to reduced stability of dislocation. In clusters the energy to create dislocation is higher than that in bulk and no dislocation was observed [Zütt00]. The formation of dislocation is always accompanied by acoustic emission (AE) [Mill87]. Such emission of acoustic wave is detected by AE technique, which is widely used to study plasticity of bulk materials. Application of AE to thin films will offer a new access to investigate the plastic behavior of thin films.

For Fe/V, the measured enthalpy change at high c_H was found to be smaller than that of bulk V, meaning the stability of MH solution is lower than that of V. The modification of hydride stability is often observed by alloying in bulk system. In case of hydrogenation of Fe-V alloy, the plateau pressure should increase [Yuka03] and the H-solubility should decrease compared to those of pure V. If intermixing of Fe and V is significant, this alloying effect possibly explains the lower stability. However, the Fe/V sample above showed the interface mixing thickness of only 0.2 ~ 0.3 nm and thus the alloying effect is of minor importance in such case of ideally prepared superlattice.

The most interesting finding concerning the H-solubility has been observed both in Fe/V and Mo/V systems. According to the investigation of H concentration by N¹⁵ method [Hjörv89], no H was detected in the V layer of 0.45 nm (= 3 ML = 3/2 unit cell of V (100) planar distance) from the Fe(Mo)/V interface. This H-depleted layer is named “dead-layer”, which is most probably caused by electron transfer from the Fe or Mo layer into the V layer [Hjörv91]. Later, Meded *et al.* [Mede05] have proposed that the origin of this dead-layer is purely ascribed to an elastic effect by rigid Fe or Mo layers. Up to now, direct proof of such layer has not been given experimentally yet. But, experimental results by ion beam measurements by different researchers on Mo/V [Hjörv91], on Nb/Fe [Nagen95] and on Nb/Cu [Yamam95] commonly suggest the existence of the dead-layer effect. More importantly, the dead-layer effect cannot ultimately be distinguished from an alloying effect, which may also cause the reduction of H-solubility.

Therefore, it is of particular interest to investigate hydrogen distribution at such heterogeneous interface, as local distribution of hydrogen is actually not known due to limited depth resolution (~ 10 nm typically, depending on the depth) of ion beam-assisted profiling of hydrogen, which is particularly called N¹⁵-method. Time-of-Flight Secondary ion mass spec-

troscopy (ToF-SIMS) [Benni94] might be strong for this purpose. However, the surface segregation of H must be completely suppressed by e.g. cryogenic cooling of sample. As discussed later, hydrogen or even deuterium is highly mobile in the metal lattice. When more energetically stable sites as sub-surface and defect sites are available, the H or D immediately diffuses to such sites. This would alter the correct distribution of H or D. Therefore, how to freeze H and D diffusion is of a major consequence concerning an analysis of these light species. This aspect in fact critically concerns in this study. When such segregation is avoided, atom probe tomography (APT) analysis [Al-K03] will open up a new way of hydrogen characterization in metals with sub-nm-resolution.

As it is already introduced above, hydrogen is highly sensitive to stress field present in the host metal lattice [Hjörv97] and, thus to the structural imperfections like dislocation, vacancy and grain boundary since hydrogen favors tensile stress around these open volume defects [Kirch88, Pundt04, Pundt06]. If these defects were present (which is usually the case in reality), hydrogen atom can be “trapped” there. Even in epitaxial thin film this interaction cannot be completely excluded. Such trapping effect then causes deviation from the linear elastic behavior as well. When *in-situ* stress measurement (e.g. cantilever method) during H-absorption [Lauda98, Nikit08] is conducted, this departure possibly is detected.

This study is motivated by the above mentioned background. Both $V_{1-x}Fe_x$ ($x = 0.02 - 0.08$) single layered film and Fe/V multi-layered film are of subjects in this study. To begin with, the $V_{1-x}Fe_x$ single layered films were studied because the hydrogenation properties and the local chemistry of V-H thin film system “at around room temperature” have not been well investigated as well for Fe/V multi-layered system. In particular, following aspects are of major interest in this study.

- (i) Stress response of $V_{1-x}Fe_x$ single layered and Fe/V multi-layered films upon hydrogen uptake (elastic and plastic properties). Departure from the linear elasticity, expected for Fe/V and for defect-H interactions.
- (ii) Local chemistry of these films with hydrogen. Establishment of new characterization method with high-resolution for H-Metal system. Proofs of dead layer.
- (iii) Interaction of hydrogen with defects (vacancies, dislocations) present in the films. New outcome by AE measurements.

To investigate these points systematically, the films were prepared with different thicknesses. Most of the films were epitaxially grown on sapphire substrates. On these films their crystal structure and interface roughness were characterized by X-ray diffraction (XRD) and X-ray reflectivity (XRR) measurement, respectively. Pole figure measurement was also conducted to investigate in-plane configuration of the films and respective epitaxial relationship was suggested. This information enables correct evaluation of results of stress measurements later on.

Hydrogen absorption behavior was monitored by electrochemical hydrogen loading and resulting equilibrium property was assessed from the shape of electromotive force (EMF) curve, which corresponds to pressure-composition isotherm (p - c - T). The results provide information about phase transition at around room temperature.

This simple H-loading technique was combined with stress measurement set up, so that the hydrogen induced in-plane stress can be simultaneously measured *in-situ*. Likewise, the structure development (H-induced lattice expansion and phase transition) was recorded by *in-situ* XRD at DESY in Hamburg, with using specially designed electrochemical H-loading cell. In corporation with Charles University in Prague, we utilized *in-situ* acoustic emission (AE) measurement during H-loading first in the world, aiming to detect hydrogen-related dislocation propagation behavior in the film. Results of these *in-situ* measurements mutually complement and one can later discuss e.g. on the presence of defect-H interaction, shift of phase boundary and onset of hydride formation.

Local microstructure and local chemistry of V and Fe/V were studied by field ion microscopy (FIM) and atom probe tomography (APT), respectively. For these analyses, films were deposited on W needle-shaped substrate. APT [Al-K03] is a strong tool especially to investigate chemistry in nm-range because of its extremely high spatial resolution (0.1 nm) in analysis direction. As this technique is based on time-of-flight measurement, all of the elements can be in principle detected. But, we used deuterium (D) instead of hydrogen in order to differentiate from residual hydrogen gas in the analysis chamber and also to suppress above addressed diffusion problem. Previous APT study by Kesten [Kest02] has detected D-distribution in V layer of Fe/V stack first in the world. However, the average D concentration was considerably lower than expected concentration. This discrepancy was later on ascribed to be D-desorption caused by exposure to air. In this study, we designed portable D₂ gas loading system to avoid this problem. In this gas loading chamber, D was introduced in the films at a controlled pressure and subsequent analysis was carried out. The evaluated D concentration was compared with that of expected

from the results of EMF measurement. Additionally, local D-distribution at Fe/V interface was investigated in relation to the existence of “dead-layer”.

This thesis consists of 7 chapters. In this chapter 1, the background and motivation of this study is described. Chapter 2 treats theoretical background of metal-hydrogen system. In chapter 3, experimental techniques used in this study are introduced. In chapter 4, results of sample characterization both on V single layer and on Fe/V multi-layer by XRD, XRR, FIM and APT are summarized. Chapter 5 introduces experimental results separately in individual sections, and shortly discusses on the results. In the results of stress measurement, emphasis is put on the influence of initial in-plane stress and initial domain size or film thickness on hydrogen-induced stress and observed deviation from the prediction by linear elasticity theory in some cases. The result of *in-situ* XRD measurement is converted to corresponding in-plane stress and comparison with those of stress measurement is made to determine phase boundaries. Thereby, hydride formation is certainly manifested. In the section of AE measurement result, increasing AE signal with increasing hydrogen concentration is successfully shown. Here, dependence of film thickness on AE is introduced. The APT section firstly introduces the influence of analysis temperature in search of correct determination of D concentration in V single layered film. Then, characterization of local D-distribution detected under proper condition is made. For Fe/V multi-layered film, the impact of D₂ pressure on the distribution as well as the average concentration of D is shown. In the last section, a symptom of dead-layer effect is introduced. In chapter 6, all of these results are globally discussed in a combined way, especially focusing on vacancy-H interaction suggested by stress measurement, plastic deformation, phase transition and occurrence of preferential site occupation. Chapter 7 summarizes this thesis.