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Zr-based Hydrogen Absorbing Films Prepared by Ion Beam Assisted Deposition[†]

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Abstract

Preparation of hydrogen absorbing thin films and evaluation of their hydrogen capacity are of great importance to develop multifunctional hydrogen absorbing composites. A linear relationship was found between the intensity of ERDA (elastic recoil detection analysis) spectrum and hydrogen content for palladium. ERDA is thus a useful tool to measure the hydrogen absorbing ability of metallic material even when the equilibrium pressure of its hydride is higher than the vacuum pressure. Zr-based films with a Mn/Zr ratio of 4.1 were successfully prepared by ion beam assisted deposition and reversibly absorbed hydrogen to reach a H/Zr atomic ratio of 2 in the hydrogen-rich region of the film when hydrided at room temperature under 100 kPa of hydrogen. The surface became rich in manganese on hydriding and the zirconium species that might capture hydrogen atoms seemed to be confined by the manganese-rich layer.

KEY WORDS: (Elastic Recoil Detection Analysis) (Hydrogen Storage Materials) (Ion Beam Assisted Deposition) (Rutherford Backscattering) (Thin Films) (Zr-based Alloys)

1. Introduction

Metal hydrides are promising materials for hydrogen storage and now being employed in nickel-hydrogen batteries. A common issue to be solved is the diminished hydrogen capacities of metal hydrides when exposed to impure hydrogen. Water and oxygen, which are present in the ambient atmosphere and are typical impurities in hydrogen, damage the hydrogen absorbing ability through formation of oxides or hydroxides on the surface.

Although sol-gel encapsulation of metal hydrides is effective to protect their properties^{1,2)}, it has a limitation inherent of the wet process. Some surface damage during the encapsulating treatment is inevitable and the hydrogen capacity tends to be lost to some extent. If the intended application extends from hydrogen storage to hydrogen separation, recovery or purification, powdery metal hydrides are not preferable. Thin films of metal hydrides covered with ceramic surface layers deposited by a certain dry process are thus required. For example, a composite film comprising metal hydride(s) and a hydrophobic ceramic shell will be used

to recover hydrogen from mixtures of hydrogen and water such as produced by water splitting on photocatalysts. The ceramic shell is to be constructed in such a manner that hydrogen is preferentially permeable with water vapor shut out.

In our previous study on Si-N films prepared by ion beam assisted deposition³⁾, sparse to dense layers of silicon nitride were successfully deposited on silicon wafers by controlling the process parameters such as Si/N transport ratio and acceleration voltage of the nitrogen ion beam. However, palladium sheet with silicon nitride deposited on its surface unexpectedly did not occlude hydrogen, probably owing to the formation of palladium silicide at the interface. Since ZrMn₂ is a good hydrogen absorber⁴⁻⁷⁾ and can be extended to multicomponent alloys⁸⁻¹²⁾, we intended to prepare Zr-Mn binary alloy films in the present work. Even if some silicidic species formed in the following step of ceramic coating, the multicomponent characteristics would favor hydrogen occlusion. Thus the purpose of the present study is to prepare Zr-based hydrogen absorbing films that are to be coated in the forthcoming work. Since ion beam assisted deposition has proved to

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be preferable in the preparation of Ti-Al intermetallic phases¹³, it is applied in the proposed synthesis. This is also because further processing will also be able to be performed in the common vacuum chamber in the future. The further processing includes not only the ceramic coating but also covering with photocatalysts to impart in situ water splitting ability.

Another purpose of the present study is to find a convenient method to evaluate the hydrogen absorbing capacities of metallic films. Although the typical volumetric method is reliable, the expected amount of occluded hydrogen is too small to be detected by the pressure change. As already demonstrated by Oya et al.¹⁴ and Jain et al.¹⁵, ERDA (elastic recoil detection analysis) is a useful tool to observe the depth profile of occluded hydrogen in films. However, it has to be confirmed that hydrogen will not desorb from the samples during the measurement under a high vacuum. In order to clarify the applicability of ERDA to hydrogen profiling, palladium hydrides with known hydrogen contents were prepared and analyzed.

2. Experimental

Zr-based thin films of 400-600 nm thickness were deposited on Si (100) substrates using an ion beam assisted deposition system¹⁶ equipped with electron-beam evaporation sources and two types of ion sources designed to operate in high-energy (2-20 keV) and low-energy (0.2-2 keV) regions. Zirconium and manganese were evaporated from respective hearths to deposit on the water-cooled substrate with an incident angle of 45° under simultaneous bombardment with argon ions. Zirconium was supplied at a rate of 0.2 nm s⁻¹ and manganese at varying rates ranging from 0.4 to 0.6 nm s⁻¹. The low-energy ion source was mainly used at 2 keV and the current density of the vertically bombarding ions was 0.1 mA cm⁻² on the substrate.

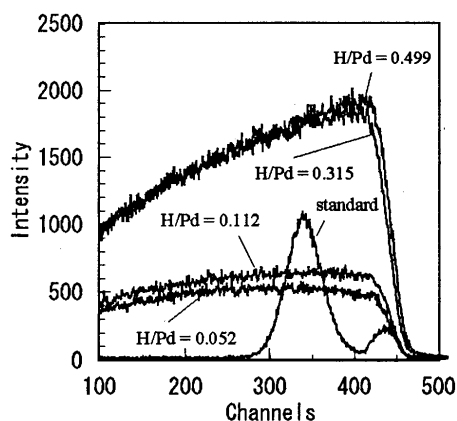


Fig. 1 ERDA spectra of palladium hydrides with varying hydrogen concentrations.

Hydriding of the Zr-based thin films was performed at room temperature under a flow of hydrogen at 100 kPa for 3 h after preheating at 623 K under 100 kPa of argon for 3 h. The dehydriding condition involved heating at 573 K for 2 h under 100 kPa of argon followed by heating at 623 K for 2 h under the same atmosphere. Commercially available sheets of palladium of 100 μm thickness were hydrided at room temperature with a Sieverts type apparatus¹⁷. Prior to hydriding the samples were washed in acetone, dried in air and evacuated at 623 K for 2 h. The extent of hydriding was adjusted by changing the pressure of admitted hydrogen and the actual H/Pd atomic ratio was volumetrically evaluated.

The elemental composition and its depth profile of the deposited films were analyzed by RBS (Rutherford backscattering spectrometry) using 2.3 MeV helium ions. ERDA experiments were performed using 3.0 MeV helium ions in the same chamber as RBS. The sample was tilted at an angle of 10° with respect to the incident helium beam direction and a detector was kept at an angle of 20° from the beam direction. A silicon wafer implanted with 40 keV hydrogen at a known dose of $1 \times 10^{17} \text{cm}^{-2}$ was used as a standard sample for ERDA.

3. Results and Discussion

3.1. Hydrogen in Palladium

The hydrogen recoil spectra taken during ERDA experiments are shown in Fig. 1. The intensity of the spectrum of hydrogen loaded palladium increased with the hydrogen content. The two distinct peaks from the standard sample were attributable to implanted hydrogen atoms and hydrogen containing surface species, respectively. The spacing between the two peaks, 114 channels, corresponded to the implanted depth, 434.7 nm. Hydrogen atoms in the palladium sheet did not reside in a limited region with specified depth, but were present over a wide region with every depth.

The spectrum of the sample with H/Pd = 0.052 was first taken and those for H/Pd = 0.112, 0.315 and 0.499 were successively recorded in this order. Since it took half an hour to obtain each of the ERDA spectra, hydrogen could be desorbed from the sample(s) evacuated for a prolonged period of time. However, such was not the case as typically shown in Fig. 2 for the sample with H/Pd = 0.052. The spectrum taken after evacuating for 2h resembled that recorded first. The equilibrium hydrogen pressure in the palladium-hydrogen binary system is 2 kPa at room temperature^{17,18}. Hydrogen in palladium should be desorbed under the high vacuum during ERDA experiment from the viewpoint of equilibrium. The

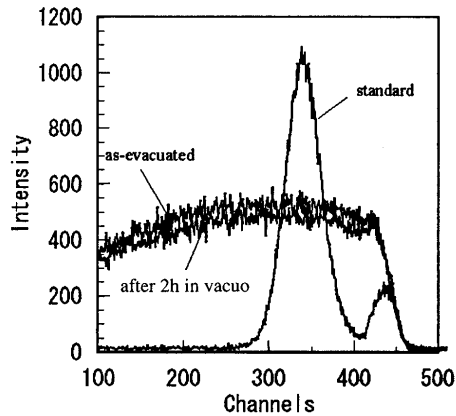


Fig. 2 Reproducibility of ERDA spectra of $\text{PdH}_{0.052}$.

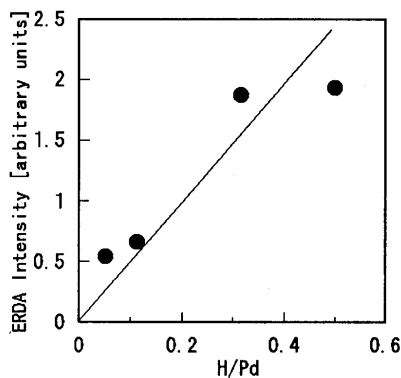


Fig. 3 Variation of ERDA intensity with hydrogen concentration.

reproducibility shown in Fig. 2 would be due to slow kinetics of hydrogen desorption and to possible hysteresis. The abovementioned equilibrium pressure is of the absorption branch and that of desorption branch might be much smaller than the former.

Figure 3 shows the linear variation of ERDA intensity with the hydrogen content. The ERDA intensity was the integrated one based upon each of the spectrum in Fig. 1. The thickness of the region that contributed to the ERDA intensity was $1 \mu\text{m}$ or so, while the H/Pd value was volumetrically observed as an averaged value throughout the whole thickness. The linear relationship suggests that absorption of hydrogen took place independently of the depth. Since the equilibrium hydrogen pressure of ZrMn_2 is similar to that of palladium, that is, 4 kPa at room temperature¹⁹⁾, and that of zirconium is much smaller²⁰⁾, the hydrogen absorbing ability of Zr-based alloys that comprise ZrMn_2 , zirconium and other phases would be well evaluated by ERDA.

3.2. Hydrogen in Zr-based Alloys

The sectional view of the as-deposited alloy film that

showed significant hydrogen absorbing ability had no significant features before hydriding as shown in Fig. 4. Grains were not observed and the as-deposited sample looked amorphous. Indeed, X-ray diffraction gave no reflection peaks. The thickness of the as-deposited film was about 600 nm. This value was somewhat larger than the expected one, 520 nm, calculated on the assumption that the film thickness was equal to the sum of the supplied amounts of the component metals with inherent densities. Although the possible sputtering effect would diminish the estimated thickness of the as-deposited film, the observed result was vice versa. It is likely that the larger thickness of the as-deposited film was brought about by some porous structure constructed through the film forming process.

Grains came to be seen on hydriding as shown in Fig. 4. Many X-ray diffraction peaks appeared to show that the hydrided sample consisted of two or more crystalline phases. The thickness of the film increased by 20% through hydriding. The extent of this expansion was nearly the same as that of the lattice volume increase of ZrMn_2 on hydriding. However, the film did not restore the initial thickness after dehydriding. The metallic atoms seemed to be displaced on hydriding, but did not change their spatial coordinates through dehydriding.

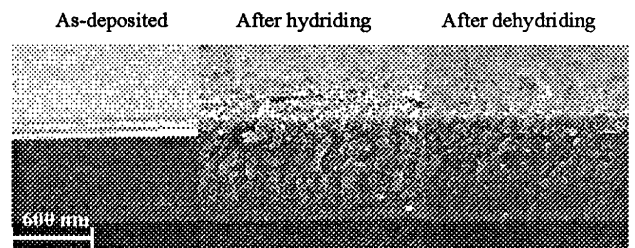


Fig. 4 SEM photographs of as-deposited and treated Zr-based films.

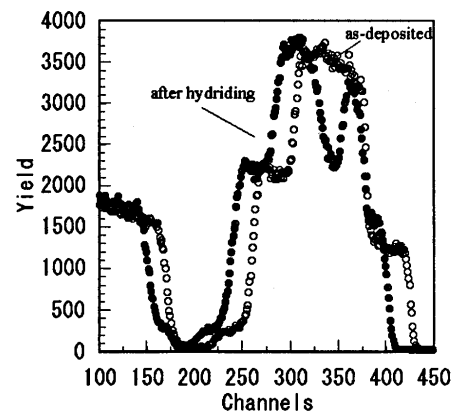


Fig. 5 RBS spectra of as-deposited and hydrided Zr-based films.

The redistribution of the metallic atoms was clearly detected by RBS as shown in Fig. 5. First of all, zirconium atoms disappeared in the surface region and the step-like profile at around channel 400 collapsed on hydriding. Secondly, a region poor in manganese formed to bring about a valley-like shape at around channel 350. Since the atomic concentrations of zirconium and manganese were independent of the depth before hydriding, the two features would have been raised by the redistribution of the components. Detailed analysis showed that the thickness of the surface region wherein zirconium became scarce was 140 nm and that the manganese-poor region spread from 180 nm to 300 nm below the surface. Zirconium seemed to move inside the film and manganese outside on hydriding.

Absorption of hydrogen by this film was significant as can be seen from ERDA spectra in Figs. 6 and 7. The region with the highest hydrogen content lay 20-30 nm below the surface and most of the occluded hydrogen atoms resided within a surface region of 190 nm thickness. The hydrogen-rich region coincided with the zirconium-poor region and the manganese-poor region did not contain hydrogen. This is apparently unusual, because zirconium is a good hydrogen absorber and

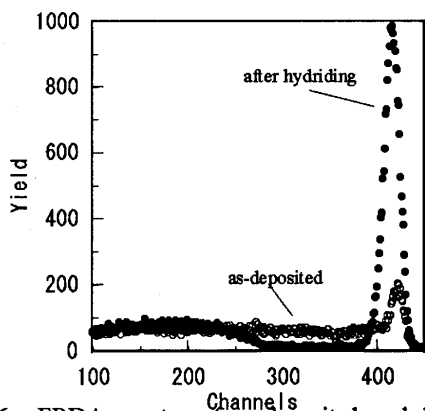


Fig. 6 ERDA spectra of as-deposited and hydrided Zr-based films.

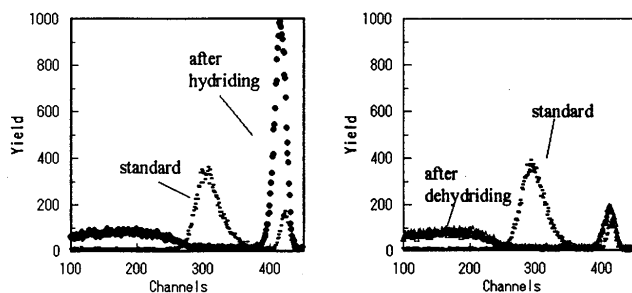


Fig. 7 Comparative ERDA spectra of hydrided and dehydrided Zr-based films.

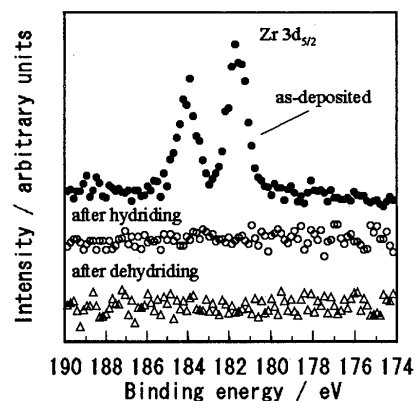


Fig. 8 XPS (photoelectron spectroscopy) spectra of as-deposited and treated Zr-based films.

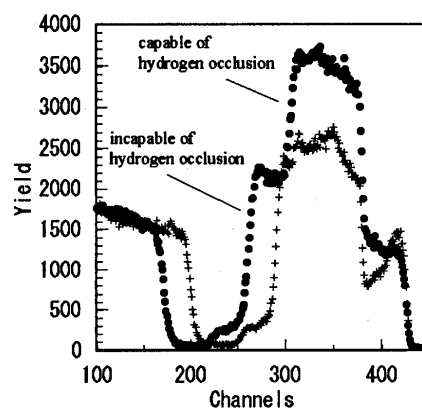


Fig. 9 Comparative RBS spectra of as-deposited Zr-based films that are capable and incapable of hydrogen occlusion.

manganese not. The total amount of occluded hydrogen was estimated to be $1.8 \times 10^{17} \text{ cm}^{-2}$ and the H/Zr atomic ratio in the hydrogen-rich region approached 2. Although this value suggested the formation of ZrH_2 , the easy dehydriding as shown in Fig. 7 contradicted this speculation. If ZrH_2 did form, hydrogen would not be desorbed during the evacuation at the mild temperature, 623 K²⁰. The reversible occlusion of hydrogen strongly suggested the formation of ZrMn_2 hydride.

The XPS results in Fig. 8 show that zirconium disappeared on the surface of the sample after hydriding and that the absence of zirconium still continued after dehydriding. This is consistent with the discussed redistribution of atoms through hydriding. It seems that driving force of atomic migration was lost once the redistribution occurred on hydriding.

The stoichiometry of the film shifted to the manganese-rich side compared to the ratio of the respective amounts of the metallic beams during

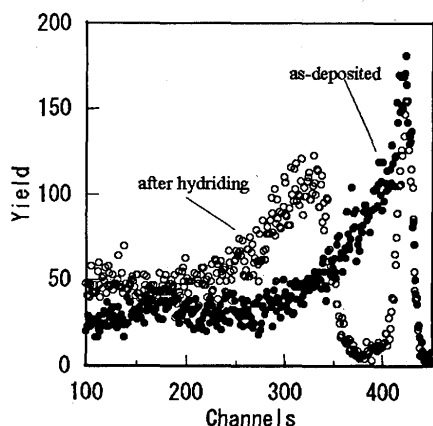


Fig. 10 ERDA spectrum change on hydriding for the Zr-based film that is incapable of hydrogen occlusion.

preparation. The sample which showed significant hydrogen absorption as discussed above had a Mn/Zr ratio of 4.1 as determined by RBS, although the supplied ratio was $Mn/Zr = 2.5$. A comparatively prepared film that had a higher Mn/Zr ratio of 4.8 as determined from the spectrum in Fig. 9 did not occlude hydrogen as shown in Fig. 10. The higher Mn/Zr ratio was brought about by intervention of some zirconium-poor region that can be seen as a dip at around channel 380 in Fig. 9. Detailed analysis of this spectrum indicated that the zirconium-poor region spread from 210 to 330 nm below the surface of the film.

It is not known why the comparatively prepared film having a higher Mn/Zr ratio did not occlude hydrogen. One explanation is that the zirconium-poor region would attract some zirconium species that could capture hydrogen atoms on hydriding. This attraction might interfere with the hydrogen absorbing action of the zirconium species that lay from the surface to about 190 nm deep. The speculative scheme of hydrogen absorption of the well-constructed sample having a proper Mn/Zr ratio of 4.1 is as follows: some zirconium species near the surface (surface to about 190 nm deep) captured hydrogen atoms dissociated on the surface, zirconium to manganese bonds were weakened and manganese atoms with lower surface energies migrated to the surface, and occluded hydrogen atoms were confined by the manganese-rich layer to be detected by ERDA.

The XPS binding energy of Zr $3d_{5/2}$ in Fig. 8 was 181.5 eV to suggest that zirconium on the surface was oxidized. Since oxidized zirconium would not occlude hydrogen and not be reduced by hydrogen, the speculative scheme discussed above would involve some manganese-assisted reduction of zirconium at the same time as the confinement. This should be evidenced by

detection of oxidation of manganese through the hydriding treatment, but as a matter of fact, manganese remained in its metallic state as observed by XPS. The proportion of oxidized manganese might be less than the detection limit.

In order to prepare a Zr-based film that has a significant hydrogen absorbing ability, zirconium should be deposited in such a manner that zirconium lying from the surface to about 200 nm deep would not diffuse to the inner region of the film without capturing hydrogen. One solution to this is a uniform distribution of zirconium. It is advisable to adjust the Mn/Zr ratio to about 4 to confine the hydrided region within manganese layer. It would be no use to raise the film thickness since the deeper region of the film would not participate in hydriding. Finally, it would be important to construct a sparse structure as discussed on the basis of the SEM photographs in Fig. 4 for hydrogen atoms to penetrate into the film.

4. Conclusion

The intensity of the ERDA spectrum for palladium hydride depended linearly on the hydrogen content. ERDA can be a useful tool to measure the hydrogen absorbing ability of a metallic material even when the equilibrium pressure of its hydride is higher than the vacuum pressure. A Zr-based film with a Mn/Zr ratio of 4.1, as determined by RBS, reversibly absorbed hydrogen. The estimated amount of hydrogen was $1.8 \times 10^{17} \text{ cm}^{-2}$ when the sample was hydrided at room temperature under 100 kPa of hydrogen. The H/Zr atomic ratio in the hydrogen-rich region approached 2. The poor abundance of zirconium in this region and the enrichment of manganese in the surface region were interpreted on the basis of a speculative hydriding scheme, where zirconium species that captured hydrogen atoms released manganese atoms and forced them to migrate to the surface.

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