Influence of Valence Band Modifications on Hydrogen Absorption in Zr-Pd Alloy Thin Films

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We study the valence band modifications of \textit{in-situ} prepared nano- and polycrystalline Pd-Zr alloy thin films using X-ray photoelectron spectroscopy. Results were compared with valence bands calculated by \textit{ab initio} methods. Furthermore, hydrogen absorption and desorption kinetics under pressure of about 570 mbar were studied in Pd covered nanocrystalline ZrPd\textsubscript{2} alloy thin film. Results showed that modifications of the valence band of the nanocrystalline alloy thin film could significantly influence on hydrogen absorption and desorption process.

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1. Introduction

Intermetallic compounds based on hydrogen absorbing elements usually also form stable hydrides. This is, for instance, the case of PdZr\textsubscript{2} alloy [1]. However, a similar compound, ZrPd\textsubscript{2} does not absorb hydrogen although both compounds have the same crystal structure and satisfy the empirical geometrical criteria for hydride formation [1]. Results of \textit{ab initio} calculations performed for ZrPd\textsubscript{2} single crystal revealed an unanticipated purely electronic origin [1].

In thin film materials dislocations and vacancies are present in higher density than in bulk material [2]. Even when the grain size is maximized by epitaxial film growth, dislocations are generated during the growth process to adjust for the lattice mismatch between the film and the substrate [3]. The local hydrogen affinity is different for these defects and therefore the materials properties are expected to be influenced by all of the mentioned microstructural components. It was shown in Ref. [4] that the valence bands of bulk nanocrystalline and nanocomposite LaNi\textsubscript{5}-based materials were broadened compared to those measured for polycrystalline samples. Furthermore, practically all of the mechanically alloyed nanomaterials showed significantly greater discharge capacity [5].

Membrane separations have potential advantages over other approaches to hydrogen purification [6–8]. Permeability calculations were performed for the potential candidates. After systematically examining all Pd-based intermetalics, no material was found to have higher hydrogen permeability than pure Pd. Moreover, it has been found very recently from theoretical calculations that ZrPd\textsubscript{2} membrane have also potentially interesting permeability [9, 10]. Therefore, modification of the electronic structure of ZrPd\textsubscript{2} films by the tuning of their microstructure could potentially improve hydrogen permeability.

In this paper, we study the electronic properties of polycrystalline and nanocrystalline Zr-Pd alloy thin films using X-ray Photoelectron Spectroscopy (XPS) and \textit{ab initio} calculations.

2. Experimental and theoretical methods

The alloy thin films were prepared in the temperature range of 295 K - 700 K using computer-controlled UHV magnetron co-sputtering [11, 12]. Pd and Zr targets were sputtered using DC and RF modes, respectively. The base pressure before the deposition process was lower than $5 \times 10^{-10}$ mbar. As a substrate we have used Si(100) wafers with an oxidised surface to prevent a silicide formation. Therefore we have applied a special heat treatment in UHV before deposition in order to obtain an epitaxial SiO\textsubscript{2} surface layer [13, 14]. The chemical composition and the cleanliness of all layers was

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checked in-situ, immediately after deposition, transferring the samples to an UHV ($4 \times 10^{-11}$ mbar) analysis chamber equipped with XPS. Details of the XPS measurements can be found in Ref. [15–17].

Furthermore, hydrogen absorption and desorption kinetics at room temperature (RT) and at a pressure of about 570 mbar were studied in ZrPd$_2$ (covered by 10 nm – Pd) thin film using four-point resistivity measurements.

The theoretical photoemission spectra are based on the electronic structures calculated with the full-potential linearized augmented-plane wave (FP-LAPW) method implemented in the WIEN2k code [18]. The method of XPS spectra calculations is discussed in more details in our previous work [19]. In this work Perdew-Burke-Ernzerhof form (PBE) [20] of the exchange-correlation potential is selected. The effective on-site Coulomb interactions parameters $U(Zr) = 2.4$ eV and $U(Pd) = 3.7$ eV [21] have been taken into account in GGA(PBE)+$U$ scheme. Plane wave cut-off parameter RK$_{max}$ is set to 8, which leads to above 500 basis functions. Relativistic effects are included with the second variational treatment of spin-orbit coupling. The total energy convergence criterion is set to $10^{-8}$ Ry. 32000 k-points is used in the whole Brillouin zone. Besides the ordered ZrPd$_2$, two simplest models of the disordered structures were considered, see Fig. 1. In these models some Zr and Pd atoms have been exchanged on sites. All three structures have been fully relaxed, which means that the volume, c/a ratio and Wyckoff positions have been optimized. The resultant lattice parameters for the ordered structure ($a = 0.347$ nm and $c = 0.8755$ nm) are about 1.8% greater than the experimental ones [22], which means a decent agreement. The theoretical XPS for a single crystal with chemical disorder is evaluated as an average of three contributions: an ordered case and two cases with antisites, see Fig. 1.

### 3. Results and discussion

In Fig. 2 we show XPS core-level spectra of the freshly deposited nanocrystalline ZrPd$_2$ alloy thin film and polycrystalline pure Pd and Zr thin films. The total thickness of the prepared thin films was about 100 nm. Due to well known high reactivity of zirconium with oxygen we have prepared the nanocrystalline alloy thin film after an additional heating of the sample holder and substrate at 700 K for 3 h and cooling to 295 K. Results showed that after such an outgassing procedure, it is possible to prepare oxygen and carbon free Zr, Pd and ZrPd$_2$ surface. In our case, the oxygen and other surface impurities are practically absent on such prepared Zr-based alloy thin films immediately after deposition. As can be seen in Fig. 2, practically no XPS signal from potential contamination atoms like O-1s and C-1s is observed.

Figure 3 shows valence bands of nano- and polycrystalline ZrPd$_2$ alloy thin films. The position of the centroids of the valence bands measured for the two samples with significantly different microstructure are practically the same. On the other hand, the XPS valence band for polycrystalline PdZr$_2$ thin film is shifted due to significantly different composition. Furthermore, valence band measured for the nanocrystalline ZrPd$_2$ is considerably broadened compared to that measured for the polycrystalline alloy thin film. The above effect could be explained by a strong deformation of the nanocrystals [15–17]. For such nanocrystalline samples the interior of the nanocrystal is constrained and the distances between atoms located at the grain boundaries are expanded.

The XPS valence band measured for polycrystalline thin film was compared with the theoretical XPS valence bands determined from ab initio calculations for single crystal with chemical disorder (Fig. 4). The average grain size measured for the polycrystalline ZrPd$_2$ thin film was
estimated as about 100 nm [23]. The two features near −2.5 and −3.8 eV observed in the theoretical XPS valence band for ideal single crystal are not detected in the experimental valence band data measured for the polycrystalline sample (see Fig. 4). This is probably as a result of stresses and grain boundaries in real polycrystalline ZrPd2 thin film.

In Fig. 5 we show relative resistivity change of the nanocrystalline 100 nm – ZrPd2 alloy thin film during hydrogen absorption and desorption at a pressure of about 570 mbar. Note that immediately after preparation the alloy thin film was covered in-situ by 10 nm Pd layer to catalyze hydrogen absorption and to protect against oxidation. The sample shows rather fast resistivity change during the first 12 s of RT absorption (see inset in Fig. 5).

On the other hand, the polycrystalline 100 nm - ZrPd2 covered by 10 nm of Pd showed practically no hydrogen absorption (resistivity change). The relatively fast absorption of hydrogen could be interesting in potential application of nanocrystalline ZrPd2 as a membrane for industrial hydrogen purification, in good agreement with recent theory [10].

In conclusions, the different microstructures observed in poly- and nanocrystalline ZrPd2 alloy thin films lead to significant modifications of their valence bands. Therefore, the nanocrystalline ZrPd2 can absorb hydrogen even below 1 bar at RT. Nanocrystalline ZrPd2 thin film materials could find potential application as a membrane for industrial hydrogen purification.

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