Electronic Properties and Bonding in ZrHₓ Thin Films Investigated by Valence-Band X-ray Photoelectron Spectroscopy

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Abstract
The electronic structure and chemical bonding in reactively magnetron sputtered ZrHₓ (x=0.15, 0.30, 1.16) thin films with oxygen content as low as 0.2 at% are investigated by 4p core-level and 3d core-level X-ray photoelectron spectroscopy. With increasing hydrogen content, we observe significant reduction of the 4d valence states close to the Fermi level as a result of redistribution of intensity towards the higher binding energies near the Fermi level. For low hydrogen content (x=0.15, 0.30), the films consist of a superposition of hexagonal closest packed metal (α-phase) and understoichiometric δ-ZrHₓ (CaF₂-type structure) phases, while for x=1.16, the film form single phase ZrHₓ that largely resembles that of stoichiometric δ-ZrH₂ phase. We show that the cubic δ-ZrHₓ phase is metastable as thin film up to x=1.16 while for higher H-contents, the structure is predicted to be tetragonally distorted. For the investigated ZrH₁.₁₆ film, we find chemical shifts of 0.68 and 0.51 eV towards higher binding energies for the Zr 4p₃/₂ and 3d₅/₂ peak positions, respectively. Compared to the Zr metal binding energies of 27.26 and 178.87 eV, this signifies a charge-transfer from Zr to H atoms. The change in the electronic structure, spectral line shapes, and chemical shifts as function of hydrogen content is discussed in relation to the charge-transfer from Zr to H that affects the conductivity by charge redistribution in the valence band.

1. Introduction
Zirconium-hydrides are important in many applications in the nuclear industry [1], in getter vacuum pumps, as hydrogen storage, in powder metallurgy, and as zircaloy [2]. The hardness, ductility and tensile strength of ZrHₓ alloys can be controlled by varying the hydrogen content [3]. Increasing the H content results in substoichiometric δ-ZrHₓ phase (CaF₂-type structure, x = ~1.6-2 [4] as shown in Fig. 1) and a body-centred tetragonal ε-phase (x = 1.75–2) with a ThH₂-type structure [5] has also been observed [4]. The δ-ZrHₓ structure originates from inserting H atoms to occupy all or parts of the tetrahedral interstitials in the CaF₂ structure. Hydrogen acts as a hardening element that prevents dislocation movements and the hydride material becomes a ceramic that is harder, but less ductile than Zr metal [6].

Traditionally, bulk Zr-hydrides are synthesized by annealing Zr metal in hydrogen gas for a time period of days to a few weeks at high temperatures between 400-900 °C for a homogeneous diffusion process at different H-contents [7]. However, defects in the bulk of the Zr metal results in variations in the diffusion rate for hydrogen that cause ZrHₓ alloys with composition gradients and less well-defined polycrystalline structure including grain boundaries. At room temperature in air, ZrHₓ quickly form a nm thin surface oxide layer that prevents further oxidation into the bulk. With increased annealing temperature, oxygen proceeds deeper into the bulk of the material, in particular along grain boundaries [8], and a few percent of oxygen
cannot be avoided with the annealing-diffusion hydration synthesis method. Consequently, the above conditions hinder adequate bonding determination in hydrides by spectroscopy.

Previous experiments on bulk ZrHₓ using ultraviolet photoelectron spectroscopy showed significant changes in the electronic structure for high hydrogen contents (x =1.63-1.94) both at the states near the Fermi level (E_F) and in deeper-lying states around -7 eV [9]. These changes were associated with a phase transition from a cubic (fcc) structure to a tetragonal (fct) structure as a result of spontaneous symmetry breaking that removes the degeneracy by a distortion known as the Jahn-Teller effect [10] that lowers the total energy of the 4d²5s² electron configuration in the Zr valence band.

For high hydrogen contents (x=1.63-1.9), core-level X-ray photoelectron spectroscopy (XPS) studies of bulk ZrHₓ materials indicated a significant shift of the Zr 4p and 3d core-levels by 1.0 eV and 0.7 eV [7], respectively. For x=1.52-1.68, valence band XPS also showed an interstitial Zr-H bonding peak around 6.4 eV below E_F [11]. Although these studies indicate significant changes in the Zr-H bond for different hydrogen contents, the spectra are affected by superimposed O 2p states that occur in the same energy region (5-8 eV) as the Zr-H bonding structures [12].

For the ZrHₓ thin films in this work, we apply XPS at the Zr 3d, 4p core-levels, and the 4d valence band to investigate the electronic structures to determine the chemical bonding and conductivity properties as a function of relatively low hydrogen content (x=0.15, 0.30, and 1.16) and compare the result to bulk α-Zr as reference. These hydride compositions were chosen to obtain a spread in the type and amount of Zr-H bonds. Deposited δ-ZrHₓ films with CaF₂-type structure, are found to be stable outside the homogeneity region determined for bulk δ-ZrHₓ with compositions ranging from about ZrH₁₅ to stoichiometric [13]. To control the structure and hence the electronic properties of the materials and to overcome the problems with oxidation, we deposited homogeneous thin films of ZrHₓ using reactive direct current magnetron sputtering (rDCMS). The thin films were grown without external heating and contamination of oxygen and other contaminants were very low. Thin films are particularly favorable for correct characterization of the material’s fundamental bonding properties and to identify different phases in understoichiometric transition metal hydrides.

2. Experimental

2.1 Thin film deposition and XRD characterization

The Zr-H films studied were deposited on Si(100) substrates by rDCMS. ZrHₓ films with x=0.15, 0.30, and 1.16 were deposited in an industrial high vacuum coating system (CemeCon AG, Würselen, Germany). Here, a zirconium target was sputtered in Ar (99.9997%)/H₂ (99.9996%) mixtures using a fixed Ar partial pressure of 0.42 Pa with 5, 10, and 20% H₂. The substrate bias was set to -80 V and no external substrate heating was applied. The films were deposited for 120 s resulting in films with thicknesses ranging between ~800 to ~840 nm. More detailed information on the deposition conditions are presented in ref [14]. The investigated α-Zr reference sample was a commercial zirconium target with a purity of 99.9% from (Kurt J. Lesker Company, Clairton, PA, USA).
2.2 XPS measurements
Valence band (VB) and XPS measurements of the Zr 3d, 4p, 4d valence band and O 1s core-level regions were performed in a surface analysis system (AXIS UltraDLD, Kratos, Manchester, U.K.) using monochromatic Al-Kα (1486.6 eV) radiation with an incidence angle of 54° and a spot size of 300 x 800 µm. The electron energy analyzer detected photoelectrons perpendicular to the sample surface with an acceptance angle of ±15°. The spectra were recorded with a step size of 0.1 eV and a pass energy of 10 eV, which provided an overall energy resolution better than 0.5 eV. The binding energy scale of all XPS spectra was referenced to the E_F, which was set to a binding energy of 0 eV [15]. The ZrH_x thin films in this work were examined before and after Ar⁺ sputtering for 600 s using an Ar⁺ incident angle of 20º at 4 keV rastered over an area of 2x2 mm².

![Zr 3d XPS spectra](image)

**Figure 2:** Zr 3d core-level XPS spectra of the ZrH_x thin films in comparison to α-Zr metal. The 3d_{5/2,3/2} spin-orbit splitting (2.41 eV) is indicated by the horizontal arrow.

2.3 Structural model and DFT Calculations
The geometry relaxation was performed using the Perdew-Burke-Ernzerhof (PBE) functional [16] including the Grimme van der Waals density functional theory (DFT)-D2 scheme [17]. The first principle calculations were carried out using density functional theory (DFT) implemented in the Vienna ab initio simulation package (VASP) [18] with an exchange-potential functional using the General Gradient Approximation (GGA). A hydrogen-potential suited for short bonds (hydrogen PAW potential H_h) with an energy cut-off of 1050 eV was used. For the self-consistent calculations, the projected augmented wave (PAW) [19] method was used with the PBE and the Heyd-Scuseria-Ernzerhof functionals of the generalized gradient approximation. The HSE06 functional [20] is a hybrid functional including a linear combination of short and long-range PBE exchange terms and a short-range Hartree-Fock term that improves the formation energies and band gaps and peak positions. The screening parameter of HSE06 was 0.2 Å⁻¹ with a plane wave cutoff energy of 700 eV. A 29x29x29 k-grid was used for the standard PBE functional for the structure relaxation and a 11x11x1 k-grid was used for HSE06 functional as the computational cost is significantly higher for the HSE06 in comparison to the PBE functional. Using the HSE06 exchange correlation functional, the energy positions of the bands are shifted by ~1.8 eV towards higher energy relative to the E_F, and are thus much more realistic, in comparison to the corresponding energy positions, using the PBE functional. The charge-transfer calculations between the different elements were made using standard BADER analysis [21].
3. Results and Discussion

Figure 2 shows Zr 3d core-level XPS spectra of the ZrHx thin films in comparison to α-Zr metal. As observed, there is a significant chemical shift towards higher binding energies for the film grown with hydrogen in the plasma compared to the pure metal film, which is a consequence of the higher electronegativity of H (χ = 2.2) in comparison to Zr (χ = 1.33) [22]. For x = 1.16, the Zr 3d5/2 peak position was determined to 179.38 eV. This is in good agreement with the Zr 3d5/2 binding energy of 179.375 eV reported for bulk δ-ZrH1.74 [23] as well as 179 eV determined for bulk ZrH1.9 material [24] and close to the 180 eV binding energy determined for bulk ZrH1.64 [25] and ZrH1.9 [7]. Furthermore, the position of the 3d5/2 peak is more or less identical to the binding energy determined for the reactively sputtered ZrH1.64 film in ref. 14 with 179.44 eV. Note the small energy shift towards lower binding energy for the less hydrogen rich film with x = 1.16 (179.38 eV) that is consistent with a smaller charge-transfer from Zr to H in this film in comparison to the x = 1.64 film (179.44 eV). In addition, for the ZrH1.16 film, there is a high-energy shift of +0.51 eV while between x = 0.15 and 0.30, the Zr 3d core-level high-energy shift is much smaller (+0.06 eV) and is an indication of smaller average charge-transfer from Zr towards H in these samples.

The metallic reference sample has the Zr 3d5/2 and Zr 3d3/2 peak positions at 178.87 and 181.28 eV (2.41 eV peak splitting) in good agreement with literature values [26]. The Zr 3d5/2 - 3d3/2 spin-orbit splitting is the same in the films. Prior to sputtering, the spectra showed structures of ZrO2 following air exposure, but at the Zr 3d-edge after sputtering there are no features connected to oxygen.

To evaluate the asymmetric tails towards higher binding energies in each spectrum, a Doniac-Sunjic function [27], corresponding to the electron-hole pair excitations created at the Fermi level to screen the core hole potential was applied. The Doniac-Sunjic profile is essentially a convolution between a Lorentzian with the function 1/E(1-α), where E is the binding energy of each peak and α is a parameter known as the singularity index that is related to the electron density of states at the Fermi level [28]. The intensities of the tails are related to the amount of metallicity in the system due to the coupling of the core-hole with collective electron oscillations. For α-Zr, the singularity index is large (α = 0.15) and the 3d5/2/3d3/2 branching ratio is higher (1.75) than the statistical value of 1.67 (5/3), signifying high conductivity. For x = 0.15...
and 0.30, the singularity index and branching ratio remains almost the same as for $\alpha$-Zr, but for $x=1.16$, the tail becomes significantly smaller with a singularity index of only $\alpha=0.04$ with a branching ratio that is smaller (1.61) than the statistical ratio (1.67). This shows that the number of bands crossing the $E_F$ are reduced and thus the expected conductivity.

Figure 3 shows Zr 4$p$ shallow core-level XPS spectra of the ZrH$_x$ thin films in comparison to $\alpha$-Zr metal. As in the case of the Zr 3$d$ level, the largest chemical shift of +0.68 eV from 27.26 eV in the metal to 27.94 eV is found for the film with $x=1.16$, while a smaller shift of 0.1 eV occurs for $x=0.30$ with a similar shift in the composition range $x=0.15$. The binding energy determined for the Zr 4$p_{3/2}$ peak of the hydride with $x=1.16$ is slightly lower than the 28.1 eV and the 28.0 eV values reported in ref. [9] and [12], respectively. For both these studies, the spectra were recorded for oxidized bulk samples, where the interaction of Zr atoms with O causes the Zr 4$p$ peak to shift to a higher binding energy. Finally, the $4p_{3/2}$ peak position of the metal reference of 27.26 eV is in agreement with the reported value of 27.1 eV in ref. [26].

Figure 4 shows a set of high-resolution VBs XPS spectra of the ZrH$_x$ thin films (0.15, 0.30 and 1.16) in comparison to $\alpha$-Zr metal. In the region 0-2 eV from the $E_F$, the spectra are dominated by the Zr 4$d$ valence states with a $4d_{5/2,3/2}$ spin-orbit splitting of ~1.3 eV, most clearly observed in pure $\alpha$-Zr ($x=0$). For $x=0.15$, the shape of the VB-XPS spectrum is very similar to that of pure $\alpha$-Zr with a larger broadening and appear to be very little affected by the small hydrogen content. On the contrary, for $x=1.16$, a major spectral redistribution of intensity changes of the shape of the Zr 4$d$ band that is further broadened so that the spin-orbit splitting is no longer resolved. The most prominent new feature appears around 6 eV binding energy and is due to

![Figure 4: Valence band XPS spectra of the ZrH$_x$ thin films in comparison to $\alpha$-Zr metal.](image-url)
the strong H 1s – Zr 4d hybridization and bonding. For x=0.30, a significant broadening of the Zr 4d valence states at ~1 eV is observed. The largest change is in the double-peaked feature between 6 and 7.8 eV. This feature is consistent with previous observations in bulk material [23] with δ-ZrH1.52, δ-ZrH1.65 and δ-ZrH1.74 where the height of the Zr 4d peak close to EF decreases and the Zr-H bonding peak increases with increasing hydrogen content. These observations suggested a donation of Zr 4d electrons towards the Zr-H bond, while the Zr-Zr bond weakens. For higher hydrogen content, (x=1.94) the states closest to the EF were enhanced due to a fcc-fct phase transition [9]. However, bulk materials are often hampered by the appearance of superimposed O 2p states between 5-10 eV i.e., in the same energy region as the Zr-H bonding peak. As ZrO2 is known to have prominent peaks of O 2p states between 5-10 eV and O 2s states around 22.5 eV from the EF [12]. Thus, in bulk materials, the contribution of the Zr-H bond peak cannot be fully distinguished or separated (disentangled) from the O 2p states due to oxygen impurities.

Figure 5 shows calculated density of states (DOS) for α-Zr and δ-ZrHx, where x=0.5, 1.0, 1.5 and 2.0. As observed, for x=0, the states within 4 eV from the EF are dominated by Zr 4d states while strong Zr 4p states occur at 29-30 eV from EF. This is also the case for increasing x but a prominent peak in the energy region 5-10 eV is mainly due to H 1s states that does not exist in pure Zr. At 5-10 eV below EF, bonding H-H s-s σ, Zr-H d-s σ and Zr-Zr d-d σ-interactions occur while antibonding H-H s-s σ* interactions appear above EF. We find that the H 1s-character in δ-ZrHx strongly depends on the hydrogen content and increases with x. Notably, a deep DOS minimum at 2-4 eV occurs for x=0.5 when hydrogen is introduced. Closer to the EF, Zr 4d-εg states dominate at 0-2 eV while H 1s-states are negligible. For δ-ZrH2, there is an intense peak at the EF of Zr 4d-1g character that dominate and cause instability of the crystal structure at 0 K. At finite temperature, phonon interactions and tetragonal (Jahn-Teller) distortion of the structure leads to a splitting of the intense t2g peak at the EF and a pseudogap develops. This leads to lowering of the total energy of the system and restabilization of the structure. Thus, the t2g states at EF are reduced at finite temperatures and likely reduces the conductivity and other transport properties. This is consistent with previous DFT studies including the δ- and ε-phases [29] [30] [31] [32] of ZrHx while comparisons to experimental electronic structure studies of the Zr-H bonds of thin films have been lacking. Thus, the order and bonding of the hydrogen atoms in the octahedral sites has not been well understood.
Figure 6 shows the structures (left) and calculated total energies (right) of ZrH\(_x\) for \(x=0.5, 1.0, 1.5\) and 2.0 (top to bottom). Here, Jahn-Teller distortion is predicted for high hydrogen content (\(x>1\)), where the cubic \(\delta\)-structure becomes unstable and lowers the symmetry. On the contrary, for low hydrogen content, the cubic structure is stable (\(x=0.5\)) or metastable (\(x=1.0\)). For \(x=2.0\), the minimum of \(c/a\) is located at 0.886, for \(x=1.5\) at 0.868 while for \(x=1\) there is a metastable state for \(c/a=1.0\) and a lowest stable state for \(c/a=0.792\). Thus, the cubic \(\delta\)-ZrH\(_x\) phase is metastable as thin film up to \(x=1.16\), while for higher H-contents, the ZrH\(_x\) structure is predicted to be distorted by the Jahn-Teller effect.

To evaluate the charge-transfer dependence on \(x\), we calculated the BADER charges that are listed in Table I together with the lattice parameters for different compositions. Unit cells of \(\delta\)-ZrH\(_x\) (Fig. 6, left panels), where the H-atoms where replaced by vacancies were used as model systems for different \(x\). Among the hydrides, the structure and stability properties of ZrH\(_2\) have been of particular interest where the attention has been focused on the \(\delta\)-\(\varepsilon\) phase transition induced by stress, and the influence of the Jahn-Teller distortion to stabilize the structure [30] [33]. As the electronegativity of Zr (1.33) is lower than for H (2.2), the formal oxidation states of H and Zr in ZrH\(_2\) are \(-1\) and \(+2\), respectively. Generally, the predicted charge-transfer from Zr increases with increasing \(x\) and lattice parameter. In comparison to the pure Zr and H elements, the Bader charge of on the Zr atoms in e.g., ZrH\(_2\) increases significantly by +1.49 e, i.e., significant charge is withdrawn from the 4d\(^2\) 5s\(^2\) valence orbitals of Zr. According to the Bader analysis of ZrH\(_2\), the charge is transferred to the lowest unoccupied orbital, of the hydrogen atoms \((1s^1\rightarrow1s^{1.75})\), where the Bader charge decreases by -0.75e on each atom. A distortion of the cubic \(\delta\)-ZrH\(_x\) structure causes a slight reduction of the charge transfer.

The combined 3d and 4p core-level and 4d valence band studies show several interesting effects. For the hydride system, we observe a significant reduction of the Zr 4d band within ~3 eV from the \(E_F\) influencing the shallow 4p core level by a broadening and an asymmetric redistribution of intensity towards higher binding energy. There is no trace of oxygen on the samples, except for \(x=0.30\) where small signs of O 2p and O 2s intensity can be distinguished. For the hydrides, a bonding band at 6 eV below the \(E_F\) does not occur in pure Zr and is related to strong H 1s – Zr 4d hybridization. This is also accompanied by a chemical shift with binding energies that are 0.6 eV higher than pure \(\alpha\)-Zr indicating significant charge-transfer towards H, in particular for \(x=1.16\). In our x-ray absorption study [34], a chemical shift towards higher energies in comparison to Zr metal was found to be due to changes in the oxidation state that depends on the structure and the formation of Zr-H bonding at sufficient hydrogen loading. Previous valence band XPS experiments have shown a dominant Zr 4d peak at 1 eV and another
peak around 6.4 eV corresponding to a Zr-H bond [35], consistent with DOS calculations [31] [29] [30]. The chemical shift of the Zr edges towards higher bonding energies confirms a significant charge-transfer from Zr towards H with increasing hydrogen content. It has been argued that a tetragonal distortion of the cubic δ-ZrH₅ structure in combination with phonons makes the structure stable [30]. However, as shown in Fig. 6, this is only the case for high H-content, while at low H-content, the cubic structure is stable or metastable and does not distort. Thus, for low H-content, the cubic δ-structure with tetrahedral Zr sites favourable affects the materials properties in comparison to a tentative octahedral coordination that for hydrogen is inhibited according to the Hägg rules on size, coordination number and electronegativity.

For ZrHₓ films deposited by rDCMS, we have previously shown that it is possible to grow films with tailored compositions by altering the concentration of H₂ in the plasma [14]. The properties of the films resemble those of the parent Zr metal where increasing hydrogen content in the films yields higher resistivity seen from the values ranging from ~70 to ~120 µΩ cm in comparison to 42.6 µΩ cm for α-Zr [36]. The measured hardness values are around 5.5 GPa, which is harder than the ~3 GPa determined for bulk α-Zr, using nanoindentation [37].

In studies of bulk ZrHₓ, there have been problems with oxide as Zr is known to slowly form stable ZrO₂ on the surface and at the grain boundaries [12]. Previous studies have thus been limited to more or less oxidized polycrystalline bulk materials that contain randomly ordered crystallites with grain boundaries that affect the results of electronic structure characterization. Moreover, investigations of the electronic structures of understoichiometric transition metal hydrides have been scarce. Thin films synthesized by reactive magnetron sputtering offer an alternative route to grow metal hydrides such as ZrHₓ with well-defined properties and at a fraction of time (deposition time of about 2 min for an 800nm film) compared to traditional hydration/percolation processes that normally takes 1-2 days or weeks depending on the H-content [7]. A further advantage of the films is the low level of contaminants, in particular, the oxygen content that is of the range of 0.2-0.7% as determined by ToF-ERDA [14]. Although 3d core-level shifts in ZrHₓ [14] has previously been observed, indicating charge-transfer from Zr to H, a deeper analysis including branching ratio and singularity index is necessary for the understanding how the electronic properties influence the conductivity. For low H-content (x=0.15 and 0.30), the films contain a mixture of metallic α-Zr and δ-ZrHₓ phases and the metallicity remains. For higher H-content (x=1.16), a homogeneous oriented, textured and understoichiometric δ-ZrHₓ phase if formed with a lower singularity index and smaller branching ratio that overall indicate more ceramic properties than for the lower H-contents. Producing highly stoichiometric and phase pure materials are thus important for optimizing electrical and hardness properties in a vast number of applications.

Conclusions

Early transition metal hydrides are a new class of thin film materials where the cubic δ-ZrHₓ phase is metastable up to x=1.16, while for higher H-contents, the ZrHₓ structure is predicted to be distorted by the Jahn-Teller effect both in thin films and bulk synthesized materials. By combining valence-band and shallow core-level X-ray photoelectron spectroscopy with electronic structure calculations, we have investigated the electronic structure and chemical bonding of ZrHₓ thin films with x=0.15, 0.30, and 1.16 in comparison to α-Zr metal. For the understoichiometric δ-ZrH₁.₁₆ film, there are significant chemical shifts of 0.68 and 0.51 eV for the 4p₃/₂ and 3d₃/₂ peak positions towards higher energies compared to the metal values of 27.26 and 178.87 eV. We find that even though there is a significant charge-transfer from the Zr 4d states towards the H 1s states in δ-ZrH₁.₁₆, there are still states crossing the Fermi level that
signifies metallicity. This is due to the fact that there is a significant asymmetric redistribution of spectral intensity from the shallow Zr 4p core-level towards the Zr 4d valence band that accompany the charge-transfer. There are important changes at the Fermi level with a splitting of the 4d band into a pseudo gap where the Fermi level is located in a local minimum that stabilize the structure and minimize the total energy of the system. For the hydrides, a bonding band around 6 eV below the Fermi level does not occur in pure Zr and is related to strong H s – Zr 4d hybridization. This is also accompanied by a chemical shift with binding energies that are 0.68 eV higher than pure α-Zr indicating significant charge-transfer towards H, in particular for x=1.16.

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