Original Paper

Electronic Structure of the Bulk of Titanium Hydrides Fractured in Ultrahigh Vacuum by XPS Surface Analysis

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The electronic structure of the fractured surface of δ-phase titanium hydrides ($TiD_{1.51}$ and $TiD_{1.93}$) with a nonstoichiometric face-centered cubic structure has been measured using X-ray photoelectron spectroscopy (XPS). It was confirmed that there exists no oxygen and carbon on the topmost fractured surface. It was clearly observed that the photoelectron peaks of Ti $2p_{3/2}$ and $2p_{1/2}$ core energy levels shifted to higher binding energies as the hydrogen content increased. The presence of new peaks in the valence band also appeared at a binding energy of around 6.4 eV. The ratio of the new peak to the Ti 3d peak increased with an increase in the hydrogen content. The growth of the new peak for titanium hydrides was interpreted by a first-principles calculation. It was revealed that the formation of hybrid orbitals comprising Ti 3d and H 1s bands and the transfer of charge from Ti 3d to H 1s occurred with an increase in the hydrogen content.

1. Introduction

The development of a hydrogen-air fuel cell comprising proton-conducting oxides that act as a solid electrolyte and hydrogen storage metals that serve as a hydrogen source has been proposed [1]. Titanium hydrides (deuterides) can potentially be used as hydrogen sources in hydrogen-air fuel cells since (1) the hydrogen migration rate, that is, the thermal diffusion, is considerably high and (2) the dissociation temperature corresponding to the potential energy that develops due to the interface between the topmost surface, made of titanium oxides, and the bulk of the hydrides is approximately 473 K [2]. Thus far, some reports on certain physical and chemical properties of titanium hydrides with various hydrogen contents have been published. However, the correlation between the electronic structure and the hydrogen content is not yet fully understood by elementary surface analyses using X-ray photoelectron spectroscopy (XPS); this is because at the topmost surface of metal hydrides, hydroxylation and oxidation occur easily due to reactions with water and oxygen [3]. In particular, hydrogen plays a significant role in catalyzing hydroxylation, oxidation, and carbonization. Even if the oxide and hydroxide layers and surface contaminants are eliminated by an ion-sputtering treatment, some surface decomposition or reduction probably occur as well [4]. Moreover, recontamination and reformation of oxide layers occur only at the topmost surface on account of ion bombardments with energies, the chemical reactivity of the surface is considerably higher than that of the bulk. Since the gradient of hydrogen distribution is also affected by sputtering, the hydrogen concentration at the surface, estimated when the specimen is prepared by hydrogenation, is not accurate.

In this study, δ-phase TiD_x (x = 1.51, 1.93) specimens having a nonstoichiometric face-centered cubic structure were prepared using a Sieverts apparatus in hydrogenation conditions wherein a D_2 gas pressure of 1.0×10^5 Pa and a heating temperature of 1073 K were maintained. The electronic structure of the bulk of the deuteride specimens, which were fractured in an ultrahigh vacuum chamber that was evacuated under a pressure of 7.8×10^{-8} Pa, was investigated by XPS surface analysis.

2. Experiments

Nonstoichiometric $TiD_{1.51}$ and $TiD_{1.93}$ were fabricated

by maintaining the same conditions for 4 hours at a hydrogen pressure of 1.0×10^5 Pa and a temperature of 1073 K, using a Sieverts apparatus. The hydrogen content was determined by mass gain, while the hydrogen pressure changes as well as the hydrogen analysis were analyzed by means of high-energy elastic recoil detection (ERD) using 2.8 MeV He^{2+} ions [5]. Since the isotopic abundance of deuterium in nature is extremely low, standing at 0.015%, and the weight of deuterium is twice that of protium, the hydrogen content can be more accurately assessed in a deuteride sample than in a hydride sample that includes protium, when the sample is subject to preparation and estimation, as mentioned above. It was confirmed by X-ray diffraction (XRD) that the hydride has a face-centered cubic structure (δ-phase) at room temperature. It was also observed by XPS and co-axial impact collision ion-scattering spectroscopy (CAI-CISS) with Ar^+ ion-sputtering at room temperature that TiO and TiO_2 layers of approximately 10 nm thickness were formed on the topmost surface of the hydride [6]. The presence of hydrogen in the hydride phase has a considerable influence on the oxidation dynamics, and oxidation occurs only on the hydride surface [3]. Moreover, a small amount of water, absorbed by the topmost surface, was observed after a direct collision of the surface with the impinging primary ions; this observation was based on topmost-surface-sensitive techniques comprising CAICISS and low-energy ERD using 2.0 keV He^+ ions [6].

To investigate the electronic structure of the hydride bulk, the surface of the hydride specimen fractured in ultrahigh vacuum was observed in situ using XPS with K-α X-rays of 1486.6 eV from an aluminum target [7]. The electronic structure of titanium metal was also observed after it was sputtered with 2 keV Ar^+ ions in order to remove surface impurities, since it is extremely difficult for metals to fracture its surface. In addition, the density of states (DOS) in several bands such as s, p, and d in the near-valence band for hexagonal Ti, cubic $TiH_{1.50}$, $TiH_{1.75}$, and $TiH_{2.00}$ were simulated using a first-principles calculation with the *ab initio* projected augmented wave (PAW) method [8].

3. Results and discussion

The electronic structure of the bulk of $TiD_{1.51}$ and $TiD_{1.93}$, fractured in ultrahigh vacuum, were observed in

situ in O 1s, C 1s, and Ti 2p core energy and valence band levels using XPS. Figs. 1(a) and 1(b) show the XPS spectra of O 1s and C 1s respectively. The electronic structure of the Ar^+ ion-sputtered surface of Ti is also plotted in Figs. 1(a) and 1(b). While oxygen and carbon are scarce on the topmost fractured surface of the hydrides, they remain on its sputtered surface of Ti. Their contaminations can not be completely removed. Figure 2 shows the XPS spectra of core-level Ti $2p_{3/2}$ and $2p_{1/2}$ for the fractured surface. The photoelectron peaks of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ for $TiD_{1.51}$ appear at binding energies of 454.4 and 460.5 eV respectively. The value of the binding energy for Ti $2p_{3/2}$ is higher than the corresponding literature [4] values for $TiH_{1.5}$, i.e.,
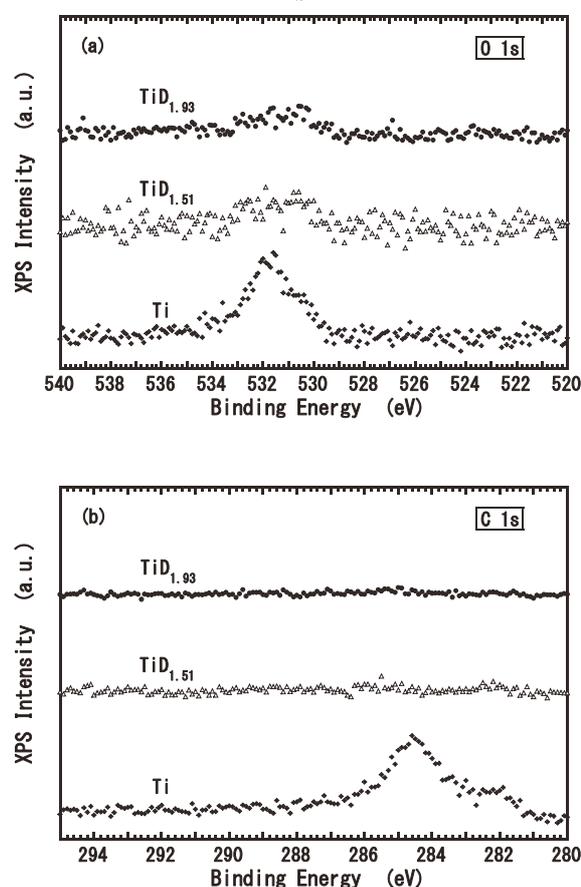

Fig. 1   XPS spectra of (a) O 1s and (b) C 1s for the fractured surfaces of $TiD_{1.51}$ and $TiD_{1.93}$, as compared with those for the Ar^+ ion-sputtered surface of Ti.

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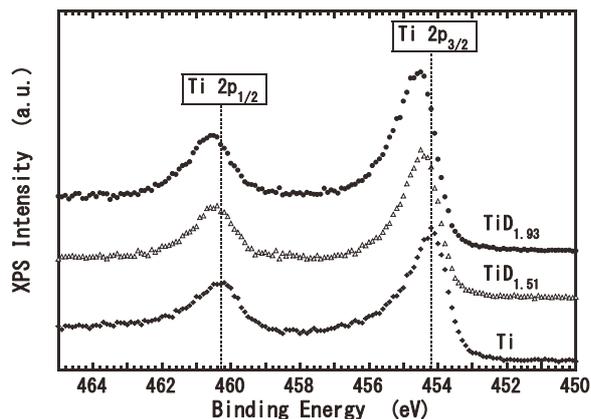*B. Tsuchiya et al.   Electronic Structure of the Bulk of Titanium Hydrides Fractured in Ultrahigh Vacuum by XPS Surface Analysis*

Fig. 2   XPS spectra of Ti $2p_{3/2}$ and $2p_{1/2}$ for the fractured surfaces of $TiD_{1.51}$ and $TiD_{1.93}$, as compared with those for the Ar$^+$-ion-sputtered surface of Ti.

approximately 453.5 eV. On the other hand, the binding energies of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ for $TiD_{1.93}$ are 454.6 and 460.6 eV, respectively. In comparison with the photoelectron peaks for Ti, which are 454.2 eV for Ti $2p_{3/2}$ and 460.3 eV for Ti $2p_{1/2}$ and show higher shifts of 1.4 eV each from the literature values of 452.8 and 458.9 eV [4], respectively, the peaks of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ shift to higher binding energies with increasing hydrogen content. This peak shift points to a slight buildup of negative charge around the hydrogen interstitials.
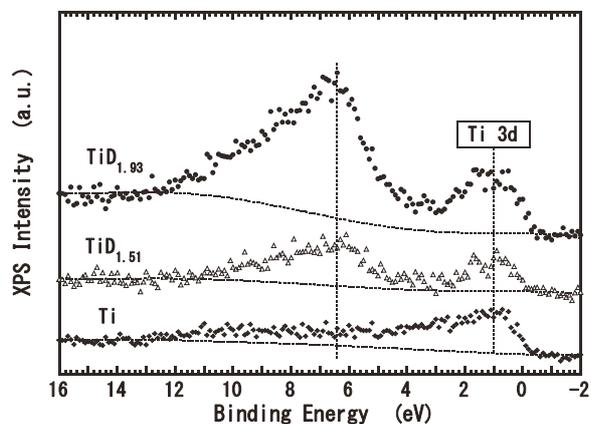

Fig. 3   Valence-band photoelectron spectra for the fractured surfaces of $TiD_{1.51}$ and $TiD_{1.93}$, as compared with those for the Ar$^+$ ion-sputtered surface of Ti.

Figure 3 shows the XPS spectra in the valence bands, including the Ti 3d band at 1.0 eV for Ti, $TiD_{1.51}$, and $TiD_{1.93}$. The 3d photoelectron peaks for $TiD_{1.51}$ and $TiD_{1.93}$ are broad and show no significant change in the presence of hydrogen in the interstices. Further, distinctive changes can be observed in Fig. 3 in that a new peak appears at around 6.4 eV below the Fermi level. The new

peak is also broad and reveals no significant change in the presence of hydrogen interstitials. It seems in Fig. 3 that the ratio of intensity of a new peak to the Ti 3d peak for $TiD_{1.51}$ is different from that for $TiD_{1.93}$. These results are in agreement with those in [4].

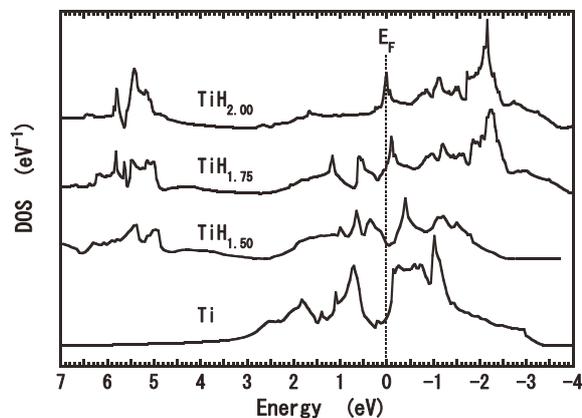Fig. 4   DOS spectra in the valence bands for Ti, $TiH_{1.50}$, $TiH_{1.75}$, and $TiH_{2.00}$.

To understand the presence of the new peak in the valence band, the DOS in binding energies of –4~7 eV for Ti, $TiH_{1.50}$, $TiH_{1.75}$, and $TiH_{2.00}$ was simulated using first-principles calculation, as shown in Fig. 4. The intensity of DOS represents the total charge of electrons per energy level in s, p, and d band states. It can be seen in Fig. 4 that there exist some new peaks in the energy region of 4.8~6.5 eV for $TiH_{1.50}$, $TiH_{1.75}$, and $TiH_{2.00}$. Moreover, no chemical shift of Ti 3d peaks for the hydrides is revealed, as compared with that for Ti. The DOS of the energy level of H1s band was also calculated using first-principles calculation. The energy level was measured at approximately 5~6 eV. The appearance of the new state may indicate toward hybrid orbitals comprising H 1s and Ti 3d band states. The ratios (I_H/I_{Ti}) of the intensity of a new peak (I_H) to that of the Ti 3d photoelectron peak (I_{Ti}) at binding energies of 5~8 eV and 0~3 eV, respectively, are shown as a function of the hydrogen content in Fig. 5. The experimental results (I_D/I_{Ti}) are also plotted in Fig. 5; these results are obtained by subtracting the background, calculated using Shirley method, from the intensity at 5~8 eV and 0~3 eV in Fig. 3. The experimental and theoretical values of I_D/I_{Ti} and I_H/I_{Ti}, respectively, increased with an increase in the hydrogen content, although their absolute values were different from each other. This result supports the theory that charge transfer from Ti 3d to H 1s is caused by the presence of hydrogen atoms.
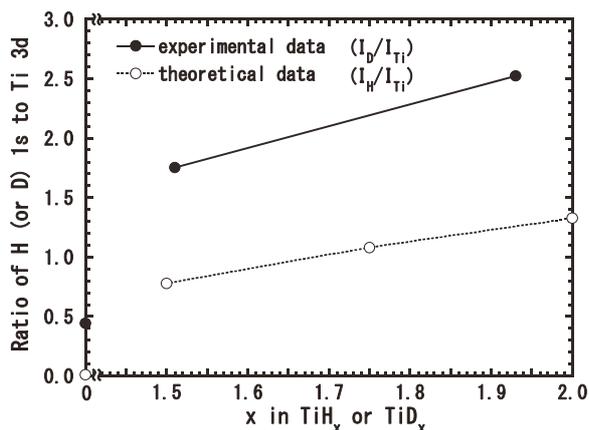
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Fig. 5   Changes in the ratios (measured by XPS and DOS) of the intensity of a new peak (I_H or I_D) to that of the Ti 3d photoelectron peak (I_{Ti}) in the binding energy regions of 5~8 eV and 0~3 eV, respectively, as shown in Figs. 3 and 4.

4. Conclusion

The electronic structure of the bulk of δ-phase $TiD_{1.51}$ and $TiD_{1.93}$, which were fractured in an ultrahigh vacuum chamber that was evacuated under a pressure of 7.8×10^{-8} Pa, was measured in situ at room temperature using XPS. The XPS spectra of the clean surface of Ti hydrides, i.e., without oxygen and carbon, were observed for the first time. The Ti $2p_{3/2}$ and Ti $2p_{1/2}$ photoelectron peaks for $TiD_{1.51}$ appear at binding energies of 454.4 and 460.5 eV, respectively, and shift to higher binding energies by approximately 0.1~0.2 eV, as compared with those for $TiD_{1.93}$. The shift in the Ti 2p core-energy level suggests a slight transfer of charge from Ti to hydrogen. In the valence band, a new peak associated with hybridized orbitals of H 1s and Ti 3d appeared at a binding energy of around 6.4 eV. The ratio of the new peak to the Ti 3d peak increased with an increase in the hydrogen content. It can be interpreted by the first-principles calculation that the growth of the new band is attributable to the migration of electrons from Ti 3d to H 1s with hydrogen in the Ti interstices.

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