nature portfolio

Peer Review File

Isotope-dependent site occupation of hydrogen in epitaxial titanium hydride nanofilms

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This paper is written about site occupation of hydrogen in epitaxial TiHx nanofilems by nuclear reaction analysis (NRA) and density functional theory (DFT) calculation. This paper clearly shows the changing of location of H and D in TiHx by NRA. NRA has enough accuracy to analyze the H or D position in Ti nanofilm and this is very powerful tool to understand the hydrogen behavior and hydrogen related phenomena in nanofilm or near surface or bulk. Although this paper includes valuable information about the site occupation of H and D, some points as shown below should consider.

1. The authors suggested that site occupation of hydrogen in epitaxial nanofilms can be controlled by changing the isotope mixture ratio and lattice strain. However, only one hybrid film ($TiH_{0.6}D_{1.0}$) was analyzed in this paper. Authors should discuss in details about D concentration dependency, what kinds of parameters can control by D. Present analysis seems to the comparison between TiHx and $TiH_{0.6}D_{1.0}$.

2. Although finding of O site occupation by H is very interesting, did the authors find any changes of properties of TiHx or TiHD by O site occupation.

3. DFT calculation showed possibility of partial O-site occupation, for example, n = 12. The authors proposed that the H deficiency assists the formation of partial O-site occupation. The authors should discuss how H deficiency affects to the stability of O-site occupation from geometrical change and electronic structure change or other effects.

4. During the DFT calculation, the lattice parameters were modified to consider the MgO interface. Lattice effect is one of the main topics in this paper. How about the lattice strain effect for stability, geometry, and electronic structure. Probably, for example, O and T site shapes or volumes may change with and without strain by MgO. This will contribute to the unique character of epitaxial nanofilm. Related to above changes, the shape of potential energy surface and ZPVE in nanofilm are also changed from no strain model.

5. In Fig.6, formation energy of Ti_8H_n was plotted with respect to the number of H in super cell (black) and x of TiHx (red). For example, right side red circle is located the 2.02? (over 2) for x of TiH_2. Why this point is not 2. Difference is only occupation site by H. number of H in cell is same. Because 16 in bottom and 2.0 in upper seems same meaning, I though black and red circle should locate same position in horizontal axis in all cases. Please check.

Reviewer #2

(Remarks to the Author)
In this paper, the site occupancy of hydrogen in titanium hydride nanofilms is analyzed using advanced measurement techniques combining NRA, RBS, etc. It is interesting to note that although the interstitial T site is the stable site for hydrogen atoms in titanium hydrides, 95% of the protium nuclei occupy the T sites (and the remaining 5% the O sites), while almost 100% of the deuterium nuclei occupy the T sites. It is commendable that such precise observations were achieved. However, there are several points that need to be clarified, mainly with regard to the computational part. The following points need to be revised before this paper can be considered for possible publication.

1. The novelty of this study should be made clearer. The academic progress that can be expected from the phenomena found in this study should also be emphasized.

2. It should be more clear what mechanism is responsible for the isotope effect on hydrogen site occupancy as found here. Is this phenomenon caused by the fact that the observation targets are epitaxial nanofilms? Also, can similar phenomena be observed for materials other than TiHx if certain conditions are met?

3. What is the margin of error for the result that 5% of hydrogen occupies the O sites?

4. Were these measurements taken at room temperature? In this paper, DFT calculations have been used to estimate the difference in hydrogen solubility energy between the T and O sites in TiH1.5: 124 meV for protium versus 151 meV for deuterium. Does this mean that this, at room temperature, results in a difference in site occupancy?

5. Since the site occupancy of hydrogen nuclei depends on temperature, an argument based solely on ZPE may overestimate (or underestimate) nuclear quantum effects.

6. The authors claim that "Therefore, the partial O-site occupation by H might be assisted by the local lattice strain." but the results of the DFT calculations presented here may not be enough to say that local strain is conducive to partial O-site occupancy.

Reviewer #3

(Remarks to the Author)
The manuscript by Ozawa et al studies in great detail, using innovative experimental means of ion channeling and nuclear reaction analysis as well as density-functional theory simulations, the locations of hydrogen and deuterium in thin films of titanium hydrides TiHx.

The main result of this manuscript is that a small percentage (estimated at 5%) of the hydrogen atoms occupy an otherwise energetically unfavorable octahedral site, with the rest of the Hydrogen atoms occupying the tetrahedral site - the one apparently occupied by the deuterium atoms.

This slight difference in occupations is explained as arising from the zero-point energy, known to be particularly large in hydrides, and estimated (from the assumed inverse mass square root dependence) to be larger for the hydride than the deuteride.

However, it is my opinion that this result and explanation do not rise to the level of noteworthiness and interest necessary for publication in a high-impact journal such as Nature Comm. A site preference of only a few percent is not noteworthy, and the subject manuscript does not present an explanation that breaks new ground. In addition, the usage of the novel experimental techniques presents, in my opinion, concerns relating to the analysis and interpretation of the experimental results. Nor is there presented a viable methodology for controlling and utilizing such occupation in the design of new materials.

For these reasons I believe this manuscript should not be published in Nature Comm.

Reviewer #4

(Remarks to the Author)
Ozama et al. have submitted a paper with the title “Isotope-dependent site occupation of hydrogen in epitaxial titanium hydride nanofilms” in which they use a combination of channeling Rutherford Backscattering Spectrometry (RBS) and Nuclear Reaction Analysis (NRA) to measure concentrations and lattice location of H and D in epitaxially grown TiH(D)x thin films. The authors also perform DFT-calculations to obtain formation energies and zero-point energies for different site occupations. The investigation of the present system investigating H and D simultaneously is novel, with similar and identical approaches earlier being used to determine lattice location and vibrational amplitude of H in bulks and recently on Iron/Vanadium superlattices. The main novel conclusion the authors draw from their experimental data in the present work is that H preferentially but not exclusively occupies tetrahedral sites, whereas D does the latter exclusively. The DFT calculations result in a difference between D and H which could yield an explanation for this observation. Additionally, authors determine thermal vibration amplitudes for H.

In general, the investigated topic and material system is interesting and further development of the employed methodology can add a highly valuable tool for analysis of hydrogen in solids.

The data presented, in particular the RBS-yields and the corresponding fits, however, is rendering the claimed results rather shaky. In comparison to results reported in ref. 31, the fit quality is much worse. This applies both to magnitude and position of features (minima and maxima) observed). Blocking would only account for the intensity - different from what is observed here.

This lack in agreement of simulations and experiment - shown only in Fig.S5 although it is the key data determining the accuracy of the approach - leaves too much uncertainties on beam parameters and other properties of the sample-system (crystallinity?) to draw such detailed conclusions such as the percentage of H and D-occupation of different lattice sites. Authors would have to show, how stable their conclusions are for significantly different fits to the RBS-data to at least partially solidify them - still the lacking symmetry etc. in the experimental data would remain.

Other issues with the manuscript:
Dechanneling by H or at least evidence for it has been observed - and should in our opinion be expected for high concentrations; deflection angles of up to 4 degrees are possible for close encounters - and deflections up to 0.1 degree expected even for rather large impact parameters on the order of 0.1Å, i.e. frequently occurring in the middle of a channel. Nevertheless, the authors claim its irrelevance. Dechanneling could be a partial explanation for deviation of RBS-yield and NEP simulations as H is present in all planes investigated (Fig S5 and 3). Contrary to blocking this would eventually affect the NRA-channeling yield. Further might the channeling yield for different planes be altered differently due to varying close encounter probability, hence might also explain the problematic fit of H-NRA peak heights with simulation of pure T occupation. The observation of reduced channeling at 45 degrees could also be explained by dechanneling.
The width in simulations does not match the experiment in Fig.4 - are the authors mapping at the correct angles?
The analysis procedure is based on separate fitting of correlated parameter (vibrational amplitude and distribution of site occupation in O and T), which increases the uncertainty of results.
It is unclear how epitaxy affects the crystal structure. Is an in-plane contraction of 4.4% compatible with the substrate lattice constant? XRD shows absolute values for lattice constants and RBS relative values. Can values of 1.6% and 2.3%, respectively, be compared?
For the determination of the MSE – which phi range was assumed? All peaks or only a few?

To conclude: without providing new experimental data and fitting simulations, we see no way to support the strong claims made in the abstract of the present work. With the data at hand, and with weakened conclusions, publication, probably in a less general journal, can be warranted as a part of the development of NRA-channeling for lattice site location in thin film systems.

Minor comments:

The stopping power in TiH – how was it obtained? What was used in the calculations?

The authors at several instances refer to Rutherford Backscattering Spectroscopy - but it is correctly termed spectrometry.

Why do the authors show the Mg-RBS signal and not the Ti-one in Fig. S2?

There is a typo in caption of Fig. S2 - Two instead of Tow

Reviewer #5

(Remarks to the Author)

Version 1:

Reviewer comments:

Reviewer #2

(Remarks to the Author)
The manuscript appears to have been carefully and properly revised. I think this paper deserves to be published in Nature Communications.

Reviewer #4

(Remarks to the Author)
Ozama et al. have resubmitted their manuscript with the title “Isotope-dependent site occupation of hydrogen in epitaxial titanium hydride nanofilms” in which they use a combination of channeling Rutherford Backscattering Spectrometry (RBS) and Nuclear Reaction Analysis (NRA) with DFT-calculations to obtain formation energies and zero-point energies to measure concentrations and lattice location of H and D in epitaxially grown TiH(D)x thin films.

In the revision the authors have addressed all specific concerns raised in the first report. The manuscript was modified accordingly, and the data evaluation improved, further corroborating the results. Additionally, the authors have made a thorough effort to explain the mixed occupation of lattice sites by more detailed detailed calculations of the electronic structure which could explain the observations by what they refer to as a “hydrogen Jahn-Teller effect”. This finding explaining the subtle deviation from expected occupancy adds significant novelty to the study, which we thus would like to recommend for publication in Nature Communications.

Reviewer #5

(Remarks to the Author)

Co-reviewed with Reviewer #4.

RESPONSE TO REVIEWERS' COMMENTS

We thank the reviewers for the time and energy expended for us. We appreciate the insightful comments about the accuracy of the analysis for the channeling experiment and the physical mechanism of partial octahedral occupation by hydrogen. In the revised manuscript, by taking into account the blocking effect in the Monte Carlo simulation, the 2D RBS pattern is well reproduced, and the reliability of the H site identification is improved, which corrects the partial occupancy of the octahedral site by H to 11%. Further DFT calculations for the electronic structures reveal that symmetry lowering due to the co-occupation of the tetrahedral and octahedral sites by H, not the epitaxial distortion from the substrate, crucially stabilizes the structure with a characteristic energy split near the Fermi level. Based on these results, we propose the concept of “hydrogen Jahn-Teller effect”. We hope these satisfy the concerns of the reviewers. Our detailed responses to the referee’s comments are as follow.

Major corrections in the revised manuscript are highlighted in yellow.
The changes in figures are as follows,

- The characterization of the sample by XRD and H depth profile by NRA was added to Fig. 1.
- The Monte Carlo simulations with and without considering the blocking effect were compared in Fig. 2.
- The H vibration amplitude was evaluated based on the two-dimensional NRA yield, not extracted line scans, in Fig. 3.
- The site occupation was also evaluated by using the two-dimensional mappings based on the several optimized simulation conditions in Fig. 4.
- DOS for TiH_2 and $TiH_{1.5}$ with different site occupation were added to Fig. 6.
- Investigation of the effect of H on the beam trajectory, calculations of zero-point energy, examination of the lattice distortion effect on the site stability were added to the supplemental material.

Reply to Reviewer #1

1. The authors suggested that site occupation of hydrogen in epitaxial nanofilms can be controlled by changing the isotope mixture ratio and lattice strain. However, only one hybrid film (TiH0.6D1.0) was analyzed in this paper. Authors should discuss in details about D concentration dependency, what kinds of parameters can control by D. Present analysis seems to the comparison between TiHx and TiH0.6D1.0.

Our experimental results show that H atoms partially occupy the O site in both $TiH_{1.47}$ and $TiH_{0.6}D_{1.0}$ films, suggesting that the H location does not depend on the isotope ratio (H/D). This is because the ZPE, whose mass dependency causes the different site occupation by H and D, naively depends on the potential shape and is almost independent of the surrounding hydrogen configuration. Therefore, D atoms are also expected to be independent of the isotope ratio, and the O site occupancy of hydrogen is expected to linearly change with the isotope ratio.

2. Although finding of O site occupation by H is very interesting, did the authors find any changes of properties of TiHx or TiHD by O site occupation.

Thank you for the beneficial comment. We carefully reexamined the electronic structures by DFT calculations. In $TiH_{1.5}$, a deep valley, so-called a pseudogap, was found in the DOS at the Fermi level at the most stable 11T1O structure (one H in the O site and the remaining 11 H atoms in the T site in Ti_8H_{12} supercell) as shown by Fig. 6(b-4). We found that this split is attributed to the nonequivalent Ti atoms due to the symmetry lowering by the partial O site occupation by H to gain the electronic energy even though the lattice energy may increase. We call this "hydrogen Jahn-Teller effect", which is a completely new concept in H-metal systems in keen contrast to the conventional Jahn-Teller effect observed in transition-metal oxides: Whereas oxygen atoms are marginally displaced (< 0.1 Å) in the oxides, H atoms are located in substantially different sites of T and O (> 1 Å) in $TiH_{1.5}$. We added these calculations and a detailed discussion on page 11 in the revised manuscript.

3. DFT calculation showed possibility of partial O-site occupation, for example, n = 12. The authors proposed that the H deficiency assists the formation of partial O-site occupation. The authors should discuss how H deficiency affects to the stability of O-site occupation from geometrical change and electronic structure change or other effects.

As mentioned above, the partial O-site occupation by H is related to the energy split near the Fermi level due to the symmetry lowering by H. From the analogy to the Jahn-Teller effect in transition-metal oxides, the position of the Fermi level in the DOS is important to gain the electronic energy. In titanium hydrides, the H deficiency results in an upward shift of the DOS in energy and a change in the Fermi level. Figure 6 shows that the energy difference between T and O sites decreases as the H deficiency increases. Therefore, the H deficiency is also an important factor to stabilize the partial O-site occupation by tuning the Fermi level as well as the symmetry lowering.

4. During the DFT calculation, the lattice parameters were modified to consider the MgO interface. Lattice effect is one of the main topics in this paper. How about the lattice strain effect for stability, geometry, and electronic structure. Probably, for example, O and T site shapes or volumes may change with and without strain by MgO. This will contribute to the unique character of epitaxial nanofilm. Related to above changes, the shape of potential energy surface and ZPVE in nanofilm are also changed from no strain model.

We thank the reviewer for useful comments. We have only considered the structures with an optimized lattice parameter and a lattice constant of -4.4% in-plane strain relative to TiH_2 in a $(\sqrt{2} \times 1 \times \sqrt{2})$ super cell to mimic the [110] termination in the original manuscript. Now, we additionally examined the strain effect in detail by calculating the total energies for the structures with various strained lattices. Fig. S11 shows the total energies of 12T and 11T1O as functions of basal lattice constants fixing the cell volume. Only a slight change in the relative stability between the 12T and 11T1O structures is observed, indicating the homogeneous lattice strain does not significantly affect the partial O-site occupation. As is pointed out by the reviewer, although the ZPE potentially varies with lattice strains, the magnitude of its change should be smaller compared to the ZPE difference between the T and O sites. In contrast, we found that the local symmetry around Ti atoms is broken in the stable 11T1O structures due to the co-occupation of tetrahedral and octahedral site by H. In the revised manuscript, therefore, we emphasize the importance of the symmetry reduction related to the H configuration rather than the epitaxial distortion.

5. In Fig.6, formation energy of Ti8Hn was plotted with respect to the number of H in super cell (black) and x of TiHx (red). For example, right side red circle is located the 2.02? (over 2) for x of TiH2. Why this point is not 2. Difference is only occupation site by H. number of H in cell is same. Because 16 in bottom and 2.0 in upper seems same meaning, I though black and red circle should locate same position in horizontal axis in all cases. Please check.

We apologize for the confusion we made. In the original manuscript, we shifted the points horizontally for eyes, so that the red and black points do not overlap. In the revised manuscript, we plotted the black and red circles at the same positions in the horizontal axis to avoid the confusion.

Reply to Reviewer #2

In this paper, the site occupancy of hydrogen in titanium hydride nanofilms is analyzed using advanced measurement techniques combining NRA, RBS, etc. It is interesting to note that although the interstitial T site is the stable site for hydrogen atoms in titanium hydrides, 95% of the protium nuclei occupy the T sites (and the remaining 5% the O sites), while almost 100% of the deuterium nuclei occupy the T sites. It is commendable that such precise observations were achieved. However, there are several points that need to be clarified, mainly with regard to the computational part. The following points need to be revised before this paper can be considered for possible publication.

1. The novelty of this study should be made clearer. The academic progress that can be expected from the phenomena found in this study should also be emphasized.

We appreciate the beneficial comments. Precise identification of the hydrogen location in samples at the atomic percent level, even in nanofilms, is the greatest advantage of the Channeling NRA. This Channeling NRA technique is also unique in that the lattice locations of the H/D isotopes are simultaneously investigated from a single sample using a single measurement because the isotopes can be distinguished by NRA. This allows us to unambiguously verify the isotope effect on the lattice location of hydrogen. With the aid of exhaustive DFT calculations, furthermore, we put forward the concept of “hydrogen Jahn-Teller effect” by examining the electronic structures. We emphasized these novelties in the revised manuscript.

2. It should be more clear what mechanism is responsible for the isotope effect on hydrogen site occupancy as found here. Is this phenomenon caused by the fact that the observation targets are epitaxial nanofilms? Also, can similar phenomena be observed for materials other than TiHx if certain conditions are met?

We estimated ZPEs more precisely based on DFT calculations in the revised manuscript. As shown in Table S2 and Fig. S10, the ZPE of hydrogen is larger at the T site than that at the O site. As for the mass dependency, ZPE is larger for H than D at any sites. These are generally understood by the dependence of ZPE on the potential shape and particle mass (m), as described by ZPE=$\frac{1}{2}\hbar\sqrt{\frac{k}{m}}$ in one-dimensional system with a potential curvature k. Hence, the energy difference between the T and O sites is larger for D, and the T site is more favored by D as schematically shown in Fig. 6. This is a scenario for the different site occupation between the two isotopes. Although other systems have not yet been investigated in this study, we expect that similar isotope-dependent site occupation can be found in different systems as long as the ZPE difference for isotopes competes with the site energy difference.

3. What is the margin of error for the result that 5% of hydrogen occupies the O sites?

We re-evaluated the beam trajectory using FLUX7. We considered the blocking effect for the back-scattered ions, which is a time-reversal process of channeling for incident ions. Furthermore, we carefully examined the beam divergence and Ti vibration amplitude in the simulations because they effectively reflect the crystallinity of samples and are in a trade-off relationship. It was found that the simulations with their several combinations reproduce the experimental data well as shown in Fig. S5. The H vibration amplitude and the O-site occupation ratio were also re-examined based on these beam conditions as shown in Figs. 3 and 4. As a result, the O-site occupation ratio was corrected to be 11 ± 2 at.%. The uncertainty was calculated using the mean and standard deviation values for the beam conditions. We added an explanation to the caption of Fig. 4.

4. Were these measurements taken at room temperature? In this paper, DFT calculations have been used to estimate the difference in hydrogen solubility energy between the T and O sites in TiH1.5: 124 meV for protium versus 151 meV for deuterium. Does this mean that this, at room temperature, results in a difference in site occupancy?

The channeling experiments were performed at room temperature. As is pointed out by the reviewer, thermal effects can increase the O-site occupancy, although the calculated energy difference between the T and O site is still too large at room temperature to thermodynamically populate the O site by H at 11 %. We would like to argue that under realistic conditions, the local symmetry can be further lowered, leading to enhancement of the hydrogen Jahn-Teller effect and stabilization of the O site. We added this discussion in the revised manuscript.

5. Since the site occupancy of hydrogen nuclei depends on temperature, an argument based solely on ZPE may overestimate (or underestimate) nuclear quantum effects.

The reviewer correctly points out that the hydrogen site occupancy should depend on temperature. Since the vibrational quantum energy of hydrogen is large compared to the thermal energy at 300 K, however, the population of higher vibrational levels can be neglected at 300 K. We note in this study the H and D locations were simultaneously identified in the channeling experiment for the $TiH_{0.60}D_{1.0}$ film, which clearly verified the isotope-dependent site occupation. This experimental result is qualitatively consistent with the calculated isotope-dependent site energies at T and O sites due to ZPE. Hence, it is reasonable to attribute the isotope-dependent site occupation to the ZPE of hydrogen.

6. The authors claim that "Therefore, the partial O-site occupation by H might be assisted by the local lattice strain." but the results of the DFT calculations presented here may not be enough to say that local strain is conducive to partial O-site occupancy.

We appreciate the critical comment. We carefully re-examined the electronic states by DFT calculations as shown in Figs. 6 and S7. It was revealed that the symmetry lowering by the H configuration stabilizes the partial O-site occupation by decreasing the electronic energy, namely the “hydrogen Jahn-Teller effect”. The displacements calculated for H atoms agrees with the off-centered H atoms observed in the channeling experiment, supporting the partial O-site occupation structure. Please also see around page 11 in the revised manuscript and the replies 2-4 to the reviewer #1 for the detail of the hydrogen Jahn-Teller effect.

Reply to Reviewer #3

The manuscript by Ozawa et al studies in great detail, using innovative experimental means of ion channeling and nuclear reaction analysis as well as density-functional theory simulations, the locations of hydrogen and deuterium in thin films of titanium hydrides TiHx.

The main result of this manuscript is that a small percentage (estimated at 5%) of the hydrogen atoms occupy an otherwise energetically unfavorable octahedral site, with the rest of the Hydrogen atoms occupying the tetrahedral site - the one apparently occupied by the deuterium atoms.

This slight difference in occupations is explained as arising from the zero-point energy, known to be particularly large in hydrides, and estimated (from the assumed inverse mass square root dependence) to be larger for the hydride than the deuteride.

However, it is my opinion that this result and explanation do not rise to the level of noteworthiness and interest necessary for publication in a high-impact journal such as Nature Comm. A site preference of only a few percent is not noteworthy, and the subject manuscript does not present an explanation that breaks new ground. In addition, the usage of the novel experimental techniques presents, in my opinion, concerns relating to the analysis and interpretation of the experimental results. Nor is there presented a viable methodology for controlling and utilizing such occupation in the design of new materials.

For these reasons I believe this manuscript should not be published in Nature Comm.

Following the constructive and insightful comments from the reviewers, we re-examined the electronic structures by DFT calculations in the revised manuscript. As is also mentioned above, it was found that the partial O-site occupation is attributed to the local symmetry lowering due to the H configuration, which decreases the electronic energy owing to the characteristic energy state with an energy split near the Fermi level. On this basis, we propose the concept of “hydrogen Jahn-Teller effect” in this paper. Our result showed that even tiny amount of hydrogen in different sites can significantly alter the electronic structures. We would like to emphasize that these findings were obtained by the precise structure analysis using the channeling NRA and the exhaustive DFT calculations. Furthermore, taking advantage of the channeling NRA for the simultaneous structure analysis of H and D from a single specimen, we revealed that H and D atoms occupy interstitial sites in a different manner, demonstrating the possibility to control the hydrogen site occupancy by the isotope effect. We believe these findings lead to a new frontier in physical properties of hydrides by tuning the hydrogen site occupation.

Reply to Reviewer #4

Ozama et al. have submitted a paper with the title “Isotope-dependent site occupation of hydrogen in epitaxial titanium hydride nanofilms” in which they use a combination of channeling Rutherford Backscattering Spectrometry (RBS) and Nuclear Reaction Analysis (NRA) to measure concentrations and lattice location of H and D in epitaxially grown TiH(D)x thin films. The authors also perform DFT-calculations to obtain formation energies and zero-point energies for different site occupations. The investigation of the present system investigating H and D simultaneously is novel, with similar and identical approaches earlier being used to determine lattice location and vibrational amplitude of H in bulks and recently on Iron/Vanadium superlattices. The main novel conclusion the authors draw from their experimental data in the present work is that H preferentially but not exclusively occupies tetrahedral sites, whereas D does the latter exclusively. The DFT calculations result in a difference between D and H which could yield an explanation for this observation. Additionally, authors determine thermal vibration amplitudes for H.

In general, the investigated topic and material system is interesting and further development of the employed methodology can add a highly valuable tool for analysis of hydrogen in solids.

The data presented, in particular the RBS-yields and the corresponding fits, however, is rendering the claimed results rather shaky. In comparison to results reported in ref. 31, the fit quality is much worse. This applies both to magnitude and position of features (minima and maxima) observed). Blocking would only account for the intensity - different from what is observed here.

This lack in agreement of simulations and experiment - shown only in Fig.S5 although it is the key data determining the accuracy of the approach - leaves too much uncertainties on beam parameters and other properties of the sample-system (crystallinity?) to draw such detailed conclusions such as the percentage of H and D-occupation of different lattice sites. Authors would have to show, how stable their conclusions are for significantly different fits to the RBS-data to at least partially solidify them - still the lacking symmetry etc. in the experimental data would remain.

We appreciate the insightful comments. We thoroughly reviewed the beam trajectory simulations. Firstly, we considered the blocking effect on RBS. Since the channeling for incoming ions is a time reversal process of the blocking for outgoing ions, the nuclear close-encounter probability of Ti (NEP(Ti)) around the <110> axis was convolved with the NEP(Ti) around the <100> axis with an energy of 2.04 MeV corresponding to the average energy of the scattered ions. Figures 2(c-1) and 2(c-2) show the calculated NEP's (Ti) with and without the correction of the blocking effect, showing that the corrected NEP(Ti) is in good agreement with the experimental Ti-RBS (Fig. 2(a)). Secondly, we carefully examined the influence of the beam divergence and Ti vibration amplitude on the beam trajectory. It was found that the simulations with their several combinations reproduce the Ti-RBS because they effectively reflect the crystallinity of samples and are in a trade-off relationship (Fig. S5). Thirdly, the H vibration amplitude and the O-site occupancy were comprehensively examined from the two-dimensional data, not extracted line scans, based on these beam conditions in Figs. 3 and 4. As a result, the reliability of the structure analysis was much improved and the value of the O-site occupation ratio by H was corrected to be 11 ± 2 at.%.

Other issues with the manuscript:
Dechanneling by H or at least evidence for it has been observed - and should in our opinion be expected for high concentrations; deflection angles of up to 4 degrees are possible for close encounters - and deflections up to 0.1 degree expected even for rather large impact parameters on the order of 0.1Å, i.e. frequently occurring in the middle of a channel. Nevertheless, the authors claim its irrelevance. Dechanneling could be a partial explanation for deviation of RBS-yield and NEP simulations as H is present in all planes investigated (Fig S5 and 3). Contrary to blocking this would eventually affect the NRA-channeling yield. Further might the channeling yield for different planes be altered differently due to varying close encounter probability, hence might also explain the problematic fit of H-NRA peak heights with simulation of pure T occupation. The observation of reduced channeling at 45 degrees could also be explained by dechanneling.
The width in simulations does not match the experiment in Fig.4 - are the authors mapping at the correct angles?

We examined the dechanneling effect due to H by calculating the NEP's(Ti) for the structures with H in the T site, H in the O site, and without H as shown in Fig. S4. The calculated NEP's(Ti) are nearly identical to each other, indicating that the effect of the H atoms on the beam trajectory need not be considered for the present experimental condition. This would be an advantage of the channeling NRA using the ^{15}N ions with relatively high incident energy. Therefore, it is fair to attribute the variation of the NRA-channeling yield to hydrogen site occupancy. The reduced channeling observed at 45 degrees might be related to the local strain rather than the dechanneling effect by H.

The figure to compare the line scans of the H-NRA and NEP(H) (originally shown in Fig. 4) is moved to Fig. S6 in the SM in the revised manuscript, where the simulations were performed in the wider range than the experiment.

The analysis procedure is based on separate fitting of correlated parameter (vibrational amplitude and distribution of site occupation in O and T), which increases the uncertainty of results.

The reviewer's point is correct in principle. However, we would like to emphasize that since most hydrogen atoms occupy the T site in the titanium hydride films, the corresponding H-NRA yield is largely determined by the H atoms at the T site. Therefore, our analytical approach, where the H vibrational amplitude at the T site was optimized first, does not undermine the accuracy of the site analysis.

It is unclear how epitaxy affects the crystal structure. Is an in-plane contraction of 4.4% compatible with the substrate lattice constant? XRD shows absolute values for lattice constants and RBS relative values. Can values of 1.6% and 2.3%, respectively, be compared?

We additionally examined the strain effect on the site stability by calculating the total energies for the structures with differently strained lattice parameters in Fig. S11, where the in-plane contraction of 4.4% corresponds to the case of perfect epitaxial growth of TiH_x film on the MgO(110) substrate. It was revealed that there is no significant change in the relative stability of the T and O sites. Rather, we found that the symmetry lowering by H related to the local strain is key to stabilization of the partial O site occupation via the hydrogen Jahn-Teller effect. According to the comment, we avoided the quantitative comparison with XRD and RBS about the lattice distortion in the revised manuscript.

For the determination of the MSE – which phi range was assumed? All peaks or only a few?
In the revised manuscript, we estimated the MSE's from the two-dimensional H-NRA mapping and NEP's(H) with the four beam conditions. The MSE calculations were performed in the limited range in the range at $\phi = -0.6 \sim 2.7°$ to avoid the effect of the sample aging by the beam irradiation.

To conclude: without providing new experimental data and fitting simulations, we see no way to support the strong claims made in the abstract of the present work. With the data at hand, and with weakened conclusions, publication, probably in a less general journal, can be warranted as a part of the development of NRA-channeling for lattice site location in thin film systems.

Minor comments:

The stopping power in TiH – how was it obtained? What was used in the calculations?
The stopping power was calculated from the lattice density and the differential scattering cross sections for Ti and H. The differential scattering cross sections for each element are given in a previous article [W.A. Lanford, in: J.R.Tesmer, M.Nastasi (Eds.), Handbook of Modern Ion Beam Materials Analysis, Materials Research Society, Pittsburgh, PA, 1995, pp.615–618].

The authors at several instances refer to Rutherford Backscattering Spectroscopy - but it is correctly termed spectrometry.
Thank you for the correction. We corrected the manuscript.

Why do the authors show the Mg-RBS signal and not the Ti-one in Fig. S2?
Ti-RBS is shown in Fig. 2(a), and Mg-RBS in Fig. S2(b).

There is a typo in caption of Fig. S2 - Two instead of Tow
We corrected the typo.

Reply to Reviewer #5
Co-reviewed with Reviewer #4.

We appreciate your insightful comments.

RESPONSE TO REVIEWERS' COMMENTS

We thank the reviewers for the time and energy expended for us. We are delighted that the scientific contribution of our study has been recognized. Your constructive and insightful suggestions have significantly improved the quality of our paper, and we deeply appreciate your thorough reviews.