

# Composition of photochromic oxygen-containing yttrium hydride films<sup>1</sup>

*Dmitrii Moldarev<sup>1-3</sup>, Daniel Primetzhof<sup>3</sup>, Chang C. You<sup>2</sup>, Smagul Zh. Karazhanov<sup>2,2</sup>, Jose Montero<sup>2</sup>, Fredrik Martinsen<sup>2</sup>, Trygve Mongstad<sup>2</sup>, Maria Ganchenkova<sup>1</sup>, Bjorn C. Hauback<sup>2</sup>, Eric S. Marstein<sup>2</sup>, Max Wolff*

<sup>1</sup>Department of Material Science, Moscow Engineering Physics Institute, Moscow, Russia

<sup>2</sup>Institute for Energy Technology, P.O. Box 40, NO-2027 Kjeller, Norway

<sup>3</sup>Department of Physics and Astronomy, Uppsala University, Box 516, SE-75120, Uppsala, Sweden

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## ABSTRACT

In this investigation, oxygen-containing yttrium hydride (YHO), prepared by reactive sputtering, with an oxygen content on the order of several ten percent due to the high reactivity of yttrium were investigated. Photochromic behavior with a dependence on deposition pressure was observed at room temperature and ambient pressure. We have accurately measured depth-resolved atomic composition profiles of photochromic YHO films to understand how the composition of the films is changed depending on deposition pressure. Films were prepared at two pressures and characterized using ion beam analysis techniques i.e. Rutherford

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<sup>2</sup> Corresponding author, e-mail: smagulk@ife.no

backscattering spectrometry and elastic recoil detection analysis. We found, that the increase of deposition pressure leads to increasing of [O]/[Y] ratio, while [H]/[Y] is reduced. Different kinetics of hydrogen release during ion beam exposure is observed. We observed a gradual increase in O concentration in the films after being exposed to ambient atmosphere over a time span of several months.

## 1. Introduction

The class of chromogenic materials is gaining attention in the scientific community due to many possible technological applications, such as smart windows in buildings, different sensors, sunglasses and visors, and displays or light modulators.<sup>1-2</sup> Although electrochromic materials are already applied in commercial devices, there are still important challenges such as response times and the high cost of fabrication and implementation. Thermochromic and photochromic materials can be applied in a much simpler design and devices are envisaged at a lower fabrication cost.

Films of the O-free yttrium hydride consisting of metallic  $\text{YH}_2$  phase and insulating  $\text{YH}_3$  phase, exhibit a photochromic effect only at high pressure.<sup>3</sup> At ambient condition, yttrium trihydride crystallizes into hexagonal lattice with  $P\bar{3}c1$  symmetry.<sup>4</sup> A phase transition into face-centered cubic (*fcc*) lattice, accompanied by a band gap closure, at a pressure of  $\sim 20$  GPa was found in first principle calculation.<sup>4</sup> Experimentally this transition was verified at 8 GPa.<sup>5</sup> Theoretical investigations have predicted that the presence of O in the  $\text{YH}_{3-x}$  lattice leads to an increased band gap and stabilization of the *fcc* lattice at ambient conditions,<sup>6</sup> which was confirmed by X-ray diffraction studies.<sup>7</sup> The material, namely oxygen-containing yttrium hydride (hereafter denominated YHO) was found to show a photochromic effect at room temperature.<sup>8</sup> The presence of large amounts of oxygen ( $[\text{O}]/[\text{Y}]$  up to 1.67) in the bulk of the YHO films deposited by reactive sputtering has been observed, by Rutherford backscattering spectrometry<sup>9</sup> (RBS) and neutron reflectometry.<sup>10</sup> Mongstad et al. found that the O atoms are evenly distributed throughout the thickness of YHO films encapsulated by a thin layer of Mo, which led to the conclusion that part of oxygen was incorporated in the films during the deposition process.<sup>9</sup> When films are not encapsulated continuous oxidation may take place while

exposed to air. For YHO, the band gap is found to depend on the deposition pressure<sup>11</sup> and to exceed 2.6 eV corresponding to the  $\text{YH}_3$  in the hexagonal structure.<sup>12</sup> Taking into account the results of theoretical studies in Ref.<sup>6</sup>, it was postulated that such a change in band gap could be related to an increase of oxygen content in the films. Such increase in band gap of rare earth hydrides had earlier been related to the oxygen content.<sup>13</sup>

In the present work, we perform a compositional analysis of YHO films to establish the effect of the deposition pressure on the film's composition and possible post-synthetic oxidation processes in air. For this purpose, we have carried out RBS and Time-of-Flight - Energy Elastic Recoil Detection Analysis (TOF-E ERDA) measurements on YHO films, synthesized by reactive sputtering on glass substrates at various deposition pressure.

## 2. Experiment

The thin films were prepared by reactive sputtering on glass substrates using a Leybold Optics A550V7 sputtering system. The deposition was carried out at room temperature in a mixed atmosphere of argon and hydrogen ( $\text{H}_2$  flux = 40 sccm; Ar flux 160 sccm) at two pressures, namely 1 Pa and 6 Pa. The nominal purity of the gases was 99.999 % for Ar and 99.9999 % for  $\text{H}_2$ . The base pressure in the sputter chamber was  $\sim 10^{-4}$  Pa prior to film deposition. A metallic yttrium target of purity 99.99% was used. The thickness of the films, measured by profilometry, was around 500 nm. More details about the deposition process can be found in Ref.<sup>14</sup>

The RBS measurements were performed with the 5 MV NEC tandem accelerator at Uppsala University. The incident particles were helium ions with an energy of 2 MeV and the

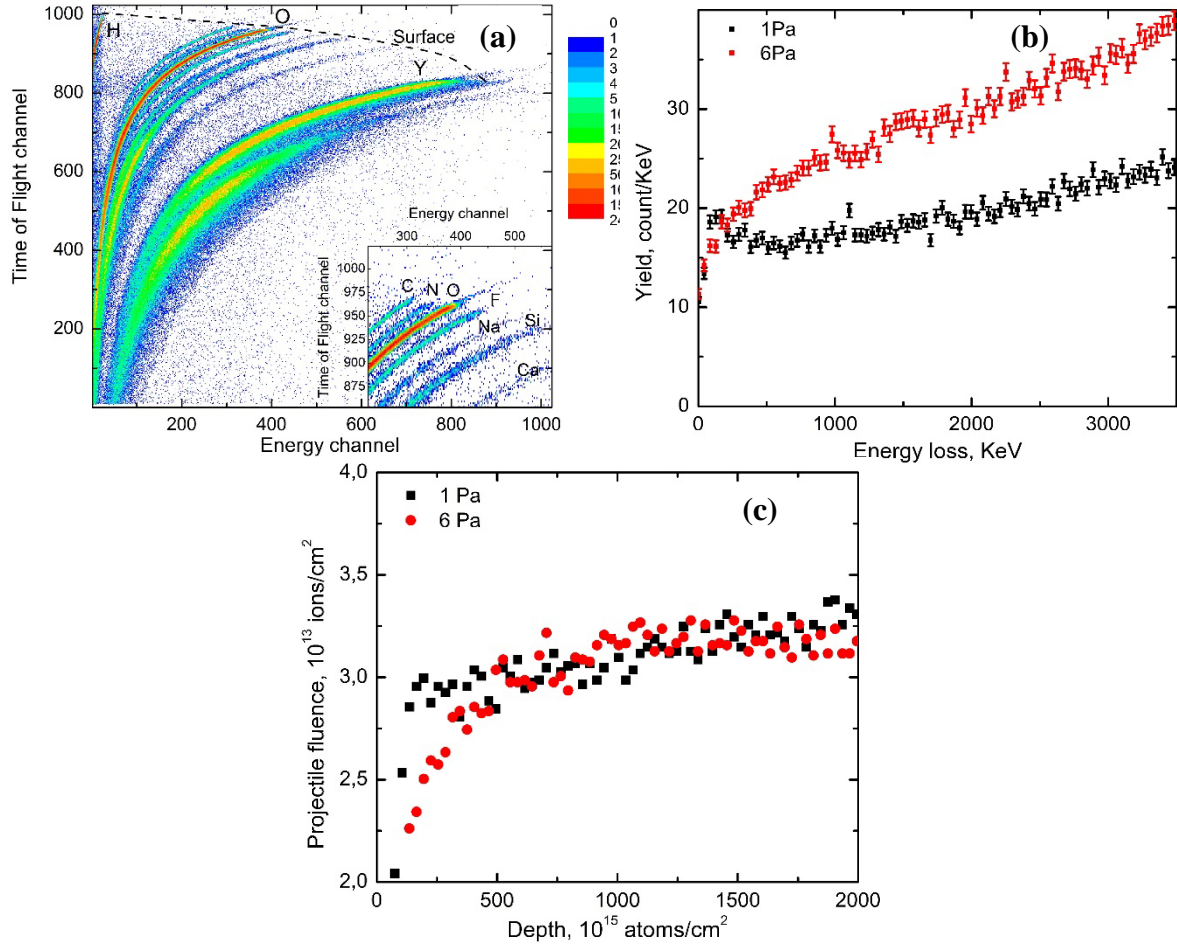
backscattered particles were detected under an angle of  $170^\circ$ . RBS spectra were analyzed by the SIMNRA software.<sup>15</sup> The TOF-E ERDA measurements were performed at the same accelerator using iodine ions with an energy of 36 MeV. The energy and TOF detectors were located at an angle of  $45^\circ$  with respect to the incident projectile direction; irradiation was performed at an angle of  $67.5^\circ$  to the surface normal of the samples. The software CONTES<sup>16</sup> was used to analyze the spectra and calculate depth profiles of each element.

### 3. Results

Figure 1 (a) shows a TOF-E ERDA coincidence spectrum for the film deposited at 1 Pa one week after deposition. Simultaneous measurements of energy (x-axis) and time of flight (y-axis) permit the separation of particles with different masses. The main constituents of the films are identified as yttrium, oxygen, and hydrogen, but traces of other chemical elements such as carbon, nitrogen, fluorine, silicon, sodium, and calcium are detected. The dashed line plotted through the high-energy edges of the curves, symbolizes the surface of the sample, while part of the curve at lower energy corresponds to signal closer to the substrate. Since the incident ions and knocked-out atoms lose energy propagating through the film. The energy loss curves for the respective elements are used for quantification of the atomic concentrations in the TOF-ERDA because the yield is proportional to concentration. Thus, the energy loss curves of the detected oxygen knocked-out atoms in Figure 1 (b) to a first approximation can be interpreted as the oxygen concentration plotted against depth. As seen from these curves, films deposited at 1 Pa show an oxygen-enriched surface layer, while the oxygen concentration below the near-surface region of the films deposited at 6 Pa is larger than that deposited at 1 Pa. Note, that the observed

increase with increasing energy loss is primarily an effect of changing scattering cross sections and stopping power, with concentration changing only marginally. With exception of oxygen, all elements are found rather uniformly distributed throughout the film thickness.

The transformation of the spectra, containing the yield knocked-out particles as a function of their energy loss into quantitative depth profile is based on the solution of a system of linear equations.<sup>17</sup> This system is solved in CONTES by a so-called inverse iteration<sup>18</sup> with projectile fluence as an adjustable parameter. Projectile fluence as a function of depth is depicted in Figure 1 (c). The actual fluence does not depend on depth, but for conversion algorithm, it is a free parameter for each depth bin and therefore can slightly deviate from constant values like it is observed for 1 Pa sample in Fig 1 (c). A significant deviation closed to the surface of the 6 Pa sample indicates the presence of high porosity at the film surface.



**Figure 1.** (a) ERDA spectrum for the film deposited at 1 Pa, (b) energy loss histograms of oxygen and (c) projectile fluence as a function of depth for the films deposited at 1 Pa and 6 Pa measured 1 week after deposition.

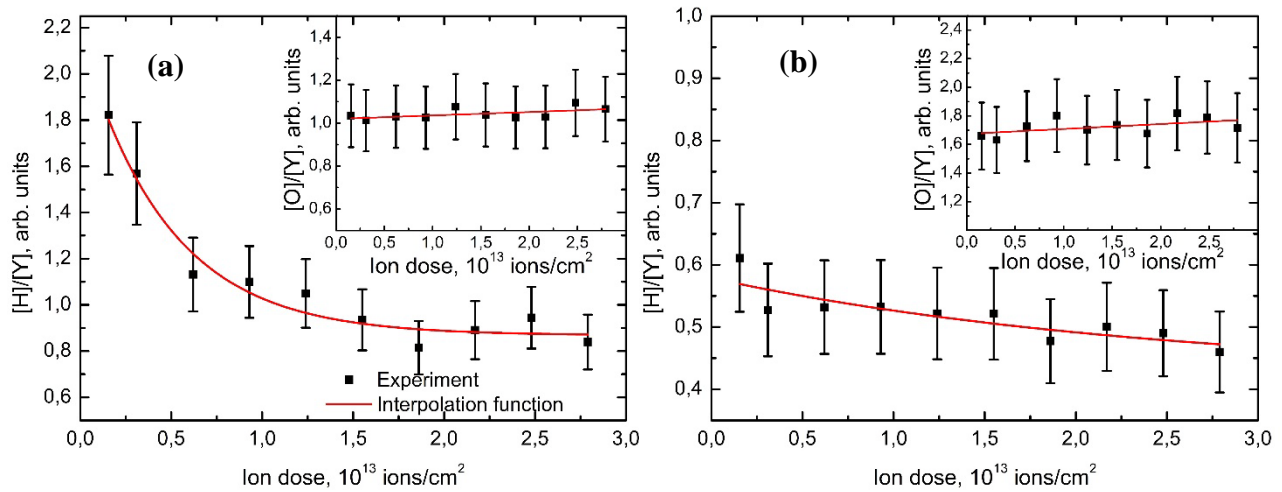
Results from TOF-E ERDA are subject to uncertainties from two main sources: first, the detection efficiency in the TOF-detector<sup>19</sup> and the unknown specific energy loss of the different detected ion lead to systematic uncertainties in derived concentrations. For heavy elements, uncertainties are found at most at 5 % of the detected concentration, whilst the uncertainties increase towards lighter elements and may significantly exceed 10-20 % of the detected

concentration of hydrogen. Note, however, that a relative comparison of the concentrations detected in different samples can be performed with much higher accuracies, as discussed in the supplements of Arvizu et al.<sup>20</sup> A second effect limiting the compositional determination in TOF-ERDA is the hydrogen depletion under heavy ion irradiation.<sup>21-22</sup> In order to account for this effect, data was recorded in list-mode to permit a dose-dependent analysis.

As expected, ERDA measurements for different primary ion dose showed different hydrogen to yttrium ratio in both 1 Pa and 6 Pa samples [Figure 2 (a, b)], whereas the oxygen to yttrium ratio remained unaffected [inset in Figure 2(a, b)]. Assuming an exponential decrease suggested in different works,<sup>23-24</sup> dose dependencies were derived and kinetic curves (red line in figure 2) were plotted. The hydrogen depletion is more pronounced in films deposited at 1 Pa than for 6 Pa: an [H]/[Y] reduction from 1.8 to 0.8 was observed after irradiation with  $3 \times 10^{13}$  ions/cm<sup>2</sup> as compared to 0.6 to 0.5 in the 6 Pa sample for similar dose. Moreover, a noticeable difference in the rate of decay is observed, that implies the lower stability of 1 Pa samples compared to the 6 Pa samples.

Using the interpolation of the kinetic curves, we find initial ratios of [O]/[Y]=1 and [H]/[Y]=2.2 for the one-week-old sample deposited at 1 Pa. An increase of the deposition pressure from 1 Pa to 6 Pa leads to an increase in the oxygen-yttrium ratio to 1.7 and to a decrease of [H]/[Y] to 0.6, i.e. concentrations of oxygen and hydrogen are anti-correlated, in agreement with the charge-neutrality argument proposed by Miniotas et al.<sup>13</sup> The total concentration of all other elements does altogether not exceed 6 % in 1 Pa samples and 8 % in 6 Pa samples.

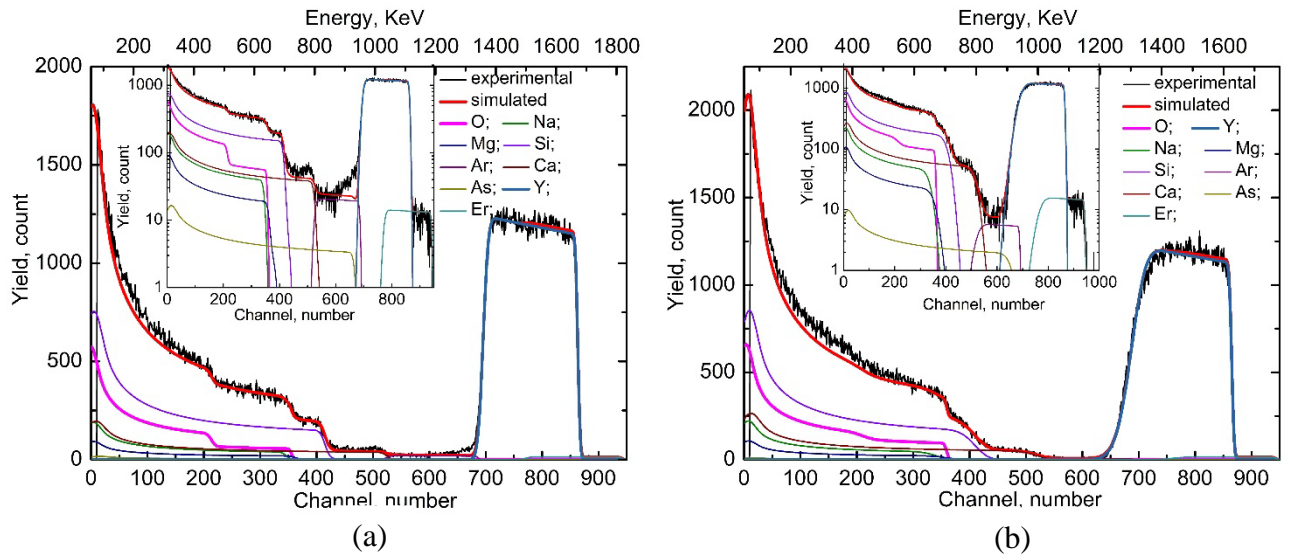




**Figure 2.** Kinetics of [H]/[Y] and [O]/[Y] ratios during ERDA measurement for films deposited at 1 Pa (a) and 6 Pa (b).

Figures 3 (a) and (b) show the results of RBS measurements for films deposited at 1 Pa and 6 Pa, respectively, 1 week after deposition. While RBS is insensitive to hydrogen, it can, for homogeneous samples yield the concentrations of Y and O and in especial the sample thickness with higher accuracy and precision than TOF-E ERDA. The ratio of the average concentration of oxygen to the average concentration of yttrium [O]/[Y] – is found to be 1 and 1.98 for the films deposited at 1 Pa and 6 Pa, respectively. The result for 1 Pa sample is consistent with the ERDA measurements, whereas the discrepancy for the 6Pa sample could be due to the roughness of the film, which makes it rather difficult to fit the oxygen in the RBS-spectrum [TABLE I]. Besides the elements detected by ERDA, the RBS data reveal the presence of a few ppm of erbium impurities in the YHO films. Moreover, the low-energy edge of the yttrium signal (Fig. 3 (b)) indicates that the observed thickness of the 6 Pa sample shows a stronger fluctuation than observed for the 1 Pa sample. This result confirms the presence of high porosity on the film surface observed by ERDA.

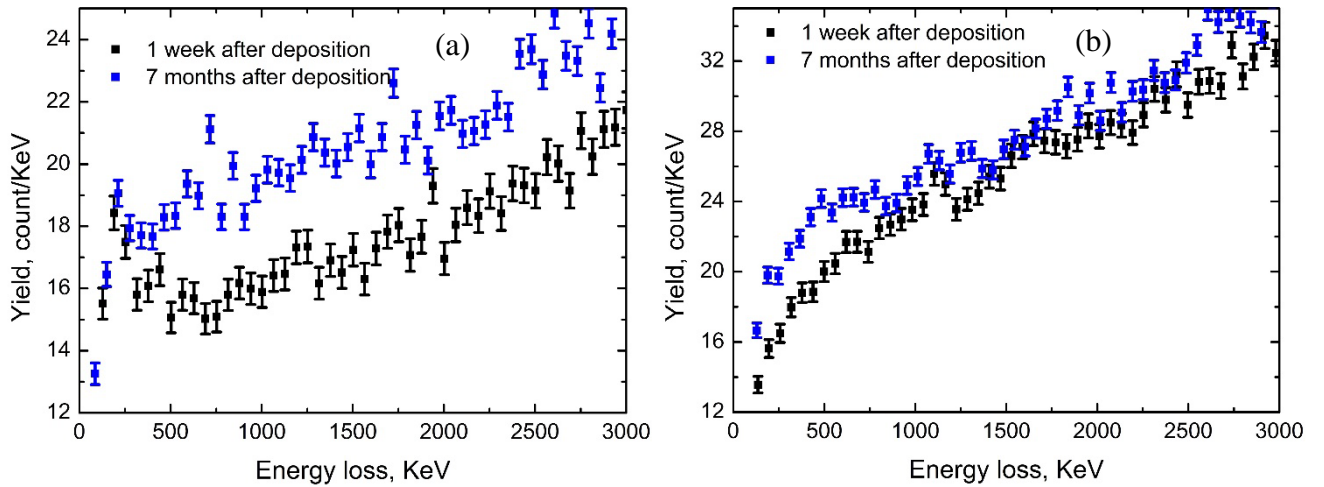
One may note that the total content of oxygen and hydrogen significantly exceeds what would be expected from the charge neutrality argument of Miniotas et al.<sup>13</sup> As an illustration, pure yttrium oxide would have an oxygen concentration of  $[O]/[Y] = 1.5$ , which is well below what is found for the 6 Pa sample, which in addition has a substantial amount of hydrogen. A reasonable explanation of this fact is that the oxygen and hydrogen to a certain extent are bound in OH-groups with one effective valence electron, as it was suggested by Mongstad et al.<sup>25</sup> based on XPS measurements.



**Figure 3.** RBS spectra for YOH films deposited on glass substrates at 1 Pa (a) and 6 Pa (b), measured 1 week after deposition.

In order to investigate the long-term stability of the samples under air exposure, ERDA measurements were repeated two and seven months after deposition [TABLE I]. Since the films were not capped with a protective layer, continuous oxidation of the films over time is expected. Energy loss histograms of oxygen in the 1 Pa sample demonstrate a higher oxygen content in the bulk seven months after deposition (Figure 3 (a)), whereas the oxygen concentration close to the

surface is not significantly altered. Therefore, it can be concluded that the oxide layer naturally formed on the surface is not completely self-passivating. For the 6 Pa sample (Figure 3(b)), the absence of the oxygen enriched layer is observed both one week after deposition and 7 months after deposition and can be related to the high porosity. Moreover, a difference in the height of the histograms over the whole energy loss range is found. The average concentration of the elements was extracted by extrapolation of the kinetic curves, see Fig. 2. As seen from TABLE I, noticeable changes in the composition occur in the films, particularly one can note an increase of oxygen concentration in both the 1 Pa and the 6 Pa samples. Taking into account anti-correlation of oxygen and hydrogen concentrations, one might expect the decrease of hydrogen concentration in the films, however, it is found to not valid in 6 Pa films.



**Figure 4.** Energy loss histograms of oxygen for the films deposited at 1Pa (a) and 6 Pa (b) measured 1 week and 7 months after deposition

**Table1.** [O]/[Y] and [H]/[Y] obtained at different times after deposition.

Deposition pressure	1 Pa			6 Pa		
	1 week	2 months	7 months	1 week	2 months	7 months
[O]/[Y]	1	1,1	1,3	1,7	2,0	2,1
[H]/[Y]	2,2	1,7	1,4	0,6	0,7	0,8

One possible explanation for the increased O concentration in the films deposited at higher deposition pressures [Fig. 1 (b)] could be an enhanced porosity, found in the films, which allows oxygen to penetrate easier into the bulk of the film during exposure to air. We have not been able to conclude on an in-situ oxygen source as proposed by Mongstad from his work with Mo-capped samples in Ref.<sup>9</sup>

In general, the observed increase in O concentration in the film deposited at higher pressure can be regarded as the main reason for the optical band gap widening observed in similar YHO films and suggested previously in Ref.<sup>11</sup> In sum, we support the attribution of optical band gap widening by oxygen, as was observed in gadolinium hydride films by Miniotas et al.<sup>13</sup>

The different kinetics of H release from the films deposited at 1 Pa and 6 Pa deposition pressures [Figs. 2 (a) and (b)] can be explained by different H concentrations in the films. The films with larger/smaller H concentration show faster/slower kinetics of H release. Another model explaining this result is based on the assumption that the release of hydrogen can be accelerated by means of a local heating due to beam exposure. Then the different kinetics of hydrogen would mean that for the 6 Pa samples hydrogen is bound in a more stable state while

the 1 Pa samples have incorporated hydrogen which is only very loosely dissolved in the material without the presence of tight chemical bonds.

## Conclusion

In summary, we have performed depth-resolved compositional analysis on oxygen-containing yttrium hydride films reactively sputtered at deposition pressures of 1 Pa and 6 Pa. Experiments are performed with ion-beam based methods, which permit an absolute quantification of all present species simultaneously, in the absence of matrix effects and the necessity of calibration samples. We have established that the oxygen concentration in YHO film is higher when the film is prepared at a higher deposition pressure. Moreover, higher deposition pressures lead to the formation of high porosity on the film surface, which might result in a higher oxygen concentration. We have shown the difference in the kinetics of hydrogen releasing under ion exposure as an indication of the difference in the sample stability. Reproducible ERDA measurements have shown an increase in the oxygen concentration in samples exposed to air over time, as a result of a gradual oxidation of the samples. Correspondingly, the hydrogen content decreases with time, suggesting an oxidation-related release of H. The weight of this evidence supports the proposition put forward of You et al.<sup>11</sup> that the oxygen content of yttrium hydride samples can be used as a handle to adjust the band gap.

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## AUTHOR INFORMATION

### **Corresponding Author**

\*(Word Style “FA\_Corresponding\_Author\_Footnote”). \* (Word Style “FA\_Corresponding\_Author\_Footnote”). Give contact information for the author(s) to whom correspondence should be addressed.

### **Present Addresses**

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## REFERENCES

1. Smith, G.; Granqvist, C., *Green Nanotechnology: Solutions for Sustainability and Energy in the Built.* **2013**.
2. Towns, A., *Applied Photochemistry: When Light Meets Molecules.* Springer International Publishing: **2016**, pp 227-279.
3. Ohmura, A.; Machida, A.; Watanuki, T.; Aoki, K.; Nakano, S.; Takemura, K., Photochromism in yttrium hydride. *Applied Physics Letters* **2007**, *91* (15), 151904.
4. de Almeida, J. S.; Kim, D. Y.; Ortiz, C.; Klintonberg, M.; Ahuja, R., On the dynamical stability and metallic behavior of YH<sub>3</sub> under pressure. *Applied Physics Letters* **2009**, *94* (25), 251913.
5. Palasyuk, T.; Tkacz, M., Hexagonal to cubic phase transition in YH<sub>3</sub> under high pressure. *Solid State Communications* **2005**, *133* (7), 477-480.
6. Pishtshev, A.; Karazhanov, S. Z., Role of oxygen in materials properties of yttrium trihydride. *Solid State Communications* **2014**, *194*, 39-42.
7. Mongstad, T.; Platzer-Björkman, C.; Karazhanov, S. Z.; Holt, A.; Maehlen, J. P.; Hauback, B. C., Transparent yttrium hydride thin films prepared by reactive sputtering. *Journal of Alloys and Compounds* **2011**, *509*, Supplement 2, S812-S816.
8. Mongstad, T.; Platzer-Björkman, C.; Maehlen, J. P.; Mooij, L. P. A.; Pivak, Y.; Dam, B.; Marstein, E. S.; Hauback, B. C.; Karazhanov, S. Z., A new thin film photochromic material:



Oxygen-containing yttrium hydride. *Solar Energy Materials and Solar Cells* **2011**, 95 (12), 3596-3599.

9. Mongstad, T. Thin-film metal hydrides for solar energy applications. Doktoravhandling. University of Oslo, **2012**.

10. Mongstad, T.; Platzer-Björkman, C.; Mæhlen, J. P.; Hauback, B. C.; Karazhanov, S. Z.; Cousin, F., Surface oxide on thin films of yttrium hydride studied by neutron reflectometry. *Applied Physics Letters* **2012**, 100 (19), 191604.

11. You, C. C.; Mongstad, T.; Maehlen, J. P.; Karazhanov, S., Engineering of the band gap and optical properties of thin films of yttrium hydride. *Applied Physics Letters* **2014**, 105 (3), 031910.

12. Huiberts, J. N.; Griessen, R.; Rector, J. H.; Wijngaarden, R. J.; Dekker, J. P.; de Groot, D. G.; Koeman, N. J., Yttrium and lanthanum hydride films with switchable optical properties. *Nature* **1996**, 380 (6571), 231-234.

13. Miniotas, A.; Hjörvarsson, B.; Douysset, L.; Nostell, P., Gigantic resistivity and band gap changes in GdOyHx thin films. *Applied Physics Letters* **2000**, 76 (15), 2056-2058.

14. You, C. C.; Mongstad, T.; Maehlen, J. P.; Karazhanov, S., Dynamic reactive sputtering of photochromic yttrium hydride thin films. *Solar Energy Materials and Solar Cells* **2015**, 143, 623-626.

15. Mayer, M., SIMNRA, a simulation program for the analysis of NRA, RBS and ERDA. *AIP Conference Proceedings* **1999**, 475 (1), 541-544.

16. Janson, M. *CONTES, Conversion of Time-Energy Spectra A Program for ERDA Data Analysis* Uppsala University: **2004**.
17. Bergmaier, A.; Dollinger, G.; Frey, C. M., Quantitative elastic recoil detection. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **1995**, *99* (1), 488-490.
18. Wilkinson, J. H., *The algebraic eigenvalue problem*. Oxford University Press, Inc.: London, **1988**.
19. Zhang, Y.; Whitlow, H. J.; Winzell, T.; Bubb, I. F.; Sajavaara, T.; Arstila, K.; Keinonen, J., Detection efficiency of time-of-flight energy elastic recoil detection analysis systems. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **1999**, *149* (4), 477-489.
20. Arvizu, M. A.; Wen, R.-T.; Primetzhofer, D.; Klemberg-Sapieha, J. E.; Martinu, L.; Niklasson, G. A.; Granqvist, C. G., Galvanostatic Ion Detrapping Rejuvenates Oxide Thin Films. *ACS Applied Materials & Interfaces* **2015**, *7* (48), 26387-26390.
21. Kenji, M.; Yuji, H., A new model for release of hydrogen isotopes from graphite. *Journal of Nuclear Materials* **1990**, *176*, 213-217.
22. Rubel, M.; Bergsåker, H.; Wienhold, P., Ion-induced release of deuterium from co-deposits by high energy helium bombardment. *Journal of Nuclear Materials* **1997**, *241*, 1026-1030.
23. Bergsåker, H.; Nagata, S.; Rubel, M., In *E-MRS Meeting XVII*, Strasbourg, **1987**.

24. Adel, M. E.; Amir, O.; Kalish, R.; Feldman, L. C., Ion-beam-induced hydrogen release from a-C:H: A bulk molecular recombination model. *Journal of Applied Physics* **1989**, *66* (7), 3248-3251.

25. Mongstad, T.; Thøgersen, A.; Subrahmanyam, A.; Karazhanov, S., The electronic state of thin films of yttrium, yttrium hydrides and yttrium oxide. *Solar Energy Materials and Solar Cells* **2014**, *128*, 270-274.

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