

Enhanced photochromic response in oxygen-containing yttrium hydride thin films transformed by an oxidation process

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Abstract

Photochromic oxygen-containing yttrium hydride (YHO) thin films with switchable optical properties have recently emerged as a promising material for the utilization in smart windows and sensor applications. In the present study, we have prepared YHO thin films with a lateral gradient of oxygen and hydrogen concentrations, which allows us to systematically investigate the effect of changes in chemical composition on their optical properties. We show that when the average lateral oxygen content exceeded a threshold level at a certain location in the as-deposited film, its appearance was abruptly changed from black opaque to yellow transparent, in which only yellow YHO exhibited photochromism. Moreover, we show that a small region (typically $\sim 5 - 10$ mm lateral size) in the black opaque part of the as-deposited film, located adjacent to the yellow transparent part of the film, was observed to transform permanently to yellow transparent upon exposure to oxygen in air in the dark for several weeks. The black to yellow color transformation was caused by an increase in the oxygen concentration, originating from the oxidation process. Optical characterization revealed pronounced photochromic response in the transformed region as compared to the rest of the yellow film. This finding demonstrates that the switchable optical properties can be tailored by changing the chemical composition of YHO films.

Keywords: Photochromism, yttrium hydride, chromogenic materials, oxidation, reactive sputtering deposition, optical properties

1. Introduction

Yttrium hydride films are well-known for their spectacular switchable optical properties: Yttrium hydride coated glass can change from a shiny mirror to a yellow transparent window during continuous absorption of hydrogen [1]. The switchable mirror effect is attractive for technological applications, such as smart windows and sensors [2]. Recently, it has been reported that yttrium hydride films also exhibit photochromism, i.e., the ability to change the optical properties by absorption of electromagnetic radiation, which is typically manifested by a reversible change of color [3, 4, 5, 6]. Such switchable optical properties are potentially interesting for smart energy-saving buildings, in which the material can be used as a coating layer on window in order to passively block unwanted incident light.

The color transition has been reported previously by Ohmura *et al.* in which an orange transparent yttrium hydride film switched to black opaque when illuminated by visible laser light under several GPa pressure at room temperature [4]. During subsequent room temperature annealing for a few hours, the black film returned to the initial orange color. Later, it has been demonstrated by Mongstad *et al.* that yttrium hydride also exhibits photochromic effect under ambient conditions [5]. The

reason for this ambient photochromism appears to be the incorporation of oxygen at the surface and in the bulk of the film. The amount of oxygen atoms was reported to be up to ~ 30 atomic % in total, as obtained by neutron reflectometry (NR) and Rutherford backscattering spectrometry (RBS) measurements [5, 7]. The NR study indicated that a surface oxide layer of 5 – 10 nm thickness formed on unprotected yttrium hydride films. By controlling the film deposition condition, it is also feasible to tune the optical band gap in such films of oxygen-containing yttrium hydride (YHO hereafter) [8]. The band gap energy of the film can be raised as a result of increased oxygen concentration, as confirmed by time-of-flight energy elastic recoil detection analysis (ToF-E ERDA) and RBS measurements [9]. In addition, the photochromic response was observed to be strongly influenced by the variation of the band gap energy. When the band gap energy of YHO films was reduced from ~ 3.7 to 2.8 eV, photochromism became more pronounced due to stronger absorption in the visible range of the light spectrum [8]. These findings indicate that the optical properties are very sensitive to the changes in chemical composition of YHO films. Hence, in order to improve and fully exploit YHO as a material for potential technological applications, it is paramount to better understand the relationship between its composition and physical properties.

In this work, we systematically investigate the effect of changes in chemical composition on the optical properties of

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YHO thin films, with a focus on photochromism. We show that by gradually varying the lateral concentrations of oxygen and hydrogen, the electrical and optical properties of the as-deposited thin films were dramatically changed.

2. Experimental

YHO thin films were reactively sputter-deposited on glass substrates by using a Leybold Optics A550V7 on-axis pulsed in-line DC magnetron sputtering machine. The size of the glass substrate is $76 \times 26 \text{ mm}^2$. A gradient in the lateral composition was achieved by keeping the substrate in a fixed position during the sputtering deposition. The total gas flow of argon and hydrogen was 200 sccm with an Ar:H₂ gas ratio of 4:1. A deposition pressure of 0.66 Pa was used. More details on the deposition conditions can be found elsewhere [8]. The as-deposited samples were annealed at room temperature and on a hotplate at 50 °C under ambient conditions. The film thickness was determined using a stylus surface profilometer. A four-point-probe was used to measure the electrical resistivity. The optical properties of the thin films were characterized using an Ocean Optics QE65000 spectrometer equipped with an integrating sphere and deuterium and tungsten halogen light sources. The spot diameter of the incident light was $\sim 5 \text{ mm}$. In order to characterize the photochromic effect, thin films were illuminated up to 24 h under artificial sunlight from a solar simulator with an intensity calibrated at 1000 W/m^2 under ambient conditions. The compositional analysis of the samples was carried out by means of ion beam techniques: ToF-E ERDA and nuclear reaction analysis (NRA), at the tandem laboratory at Uppsala university in Sweden. In case of ERDA, iodine ions with an energy of 36 MeV were used as primary particles. The measurements were performed using the following geometry: The angle between the incident ion beam and the surface normal of the sample was 67.5°; the angle between incident ion beam and detectors was 45°. To convert obtained spectra into composition of films and depth profile of the elements, the software CONTES was used[10]. NRA was performed using following nuclear reaction: $^{15}\text{N} + ^1\text{H} \rightarrow ^{12}\text{C} + ^4\text{He} + \gamma$ (4.43 MeV), in order to validate the hydrogen concentration in the films [11]. The energy of the incident ^{15}N ions was typically scanned from 6.38 to 7 MeV. A TaH sample with known hydrogen concentration was prepared to calibrate NRA measurements.

3. Results and discussion

Representative photographs of a YHO thin film are shown in Fig. 1. The film thickness was 750 nm in the black region (measured at the left corner of the sample) and 800 nm in the yellow region (right corner). The thickness gradient across the lateral direction shows that the deposition rate was higher for the yellow film as compared to the black film. The red line marks the initial boundary between the black and yellow parts of the as-deposited film. The electrical resistivity varied from $\sim 10^{-2}$ in the black opaque region to $10^6 \text{ }\Omega\text{cm}$ in the yellow transparent region. The transformation of the black opaque film adjacent to

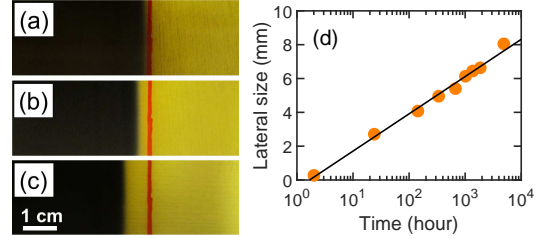


Figure 1: Representative photographs of a YHO thin film captured after (a) 2 h, (b) 24 h, and (c) 57 days after deposition. The same sample was exposed to oxygen in air in the dark at room temperature over several weeks. The red line depicts the initial boundary between the black and yellow parts of the as-deposited film. As the film was exposed to oxygen, the black opaque film close to the boundary was observed to slowly change to yellow transparent. (d) Lateral size of the transformed region plotted as a function of oxygen exposure time. The transformation rate can be described by a logarithmic function, as indicated by the black line.

the yellow transparent region is vividly illustrated in Fig. 1(a), (b), and (c), which were captured from the same sample 2 h, 24 h, and 57 days, respectively, after the film was removed from the sputter chamber. As can be seen, the lateral size of the transformed region increased continuously to $\sim 6.5 \text{ mm}$ upon exposure to oxygen in air in the dark at room temperature for 57 days. The evolution of the black to yellow color transformation was monitored over a time span of almost 7 months, as displayed in Fig. 1(d). As shown, the transformation rate can be described by a logarithmic function represented by the black line, indicating that the change of color and transparency in the film was relatively fast in the beginning, which then became very slow after some time. It should be pointed out that the black to yellow color transformation rate could be accelerated by heating. The transformation rate was found to be about 10 times faster during the first 2 h when the film was annealed on a hotplate at 50 °C in air. In general, the black to yellow color transformation appears to be dependent on the environment. When a YHO film was stored in an oxygen-depleted environment, such as in a glove box filled with nitrogen gas (humidity below 0.1 ppm), the color transformation rate was observed to be approximately 40% slower than a film stored in air (humidity of $\sim 25\%$) over a period of 6 days. However, the resulting transformed color observed in the glove box was noticeably darker (i.e., dark yellow) as compared to the yellow color seen in air.

In order to gain insight into the physical mechanism responsible for the permanent transformation from black opaque to yellow transparent in the YHO thin film during continuous oxygen exposure, the chemical composition of the film needs to be addressed. The normalized and interpolated ERDA maps in Fig. 2(a) and (b) show the qualitative distribution of oxygen and hydrogen contents in a YHO thin film sample, respectively. ERDA measurements were performed 21 days after sample deposition. Note that the red line denotes the position of the initial boundary between the black and yellow parts of the as-deposited film, while the black line represents the new position obtained at the actual time of measurements. As can be seen, the main trend is that the oxygen and hydrogen concentrations

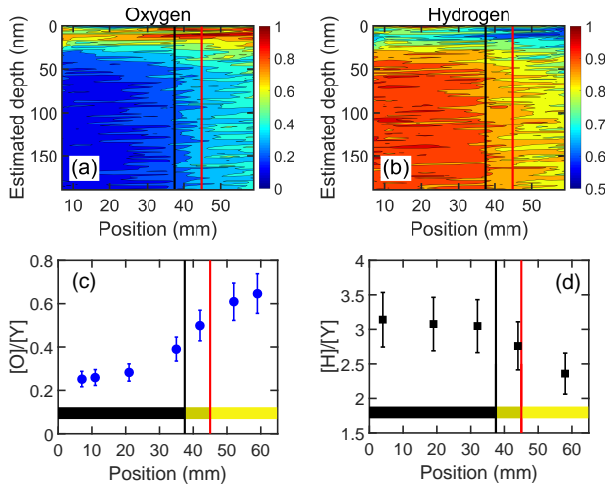


Figure 2: Normalized and interpolated ERDA maps of oxygen (a) and hydrogen (b) contents in a YHO thin film obtained 21 days after deposition, displaying the qualitative atomic distribution in the film. Average bulk $[O]/[Y]$ (c) and $[H]/[Y]$ (d) ratios plotted as a function of lateral measurement position. The red and black lines denote the boundary positions of the black and yellow parts of the film right after deposition and at the actual time of measurements, respectively. The transformed region in the middle is shown by the dark yellow color in (c) and (d).

varied considerably in the lateral direction of the film. In addition, we observed an oxygen-enriched and hydrogen-depleted surface layer as shown by the ERDA maps. The thickness of the oxygen-enriched surface layer was on the order of 5 – 10 nm. In the bulk of the film, however, oxygen appeared to be almost evenly distributed throughout the scanning depth. These results are consistent with our previous findings in similar films [7]. Average bulk $[O]/[Y]$ and $[H]/[Y]$ ratios as a function of lateral measurement position are displayed in Fig. 2(c) and (d), respectively. The atomic concentration at a given position was averaged over a volume corresponding to the ion beam probe area size multiplied by the scanning depth, excluding the surface layer. We observed a significant increase in $[O]/[Y]$ when moving from the black to the yellow part of the film, which was accompanied by a decrease in $[H]/[Y]$. In the black opaque part of the film, the average $[O]/[Y]$ ratio increased gradually from 0.25 to 0.39 when approaching the transformed region. In the transformed region, $[O]/[Y]$ raised to approximately 0.5, which may be considered as a measure for a threshold oxygen level in order for the black to yellow color transformation to take place upon oxidation under ambient conditions. In the yellow transparent region, $[O]/[Y]$ increased further to 0.65. In contrast, the average $[H]/[Y]$ ratio reduced gradually from 3.1 down to 2.4 at the same time. Such high $[H]/[Y]$ ratios imply that OH complexes may be present in the sample, especially in the black opaque part, in order to achieve charge neutrality for the yttrium atoms which have a formal valence of +3 [12].

The optical properties of YHO thin films were strongly influenced by the changes in the chemical composition, as shown in Fig. 3 and 4. The optical transmission and absorption of a YHO sample, acquired at measurement positions of 10, 40, and 70 mm, are presented in Fig. 3(a) and (b), respectively.

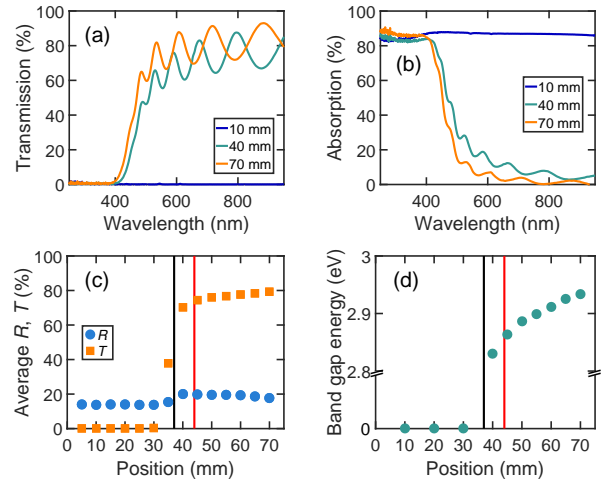


Figure 3: Transmission (a) and absorption (b) data for a YHO thin film sample obtained at three lateral positions of 10, 40, and 70 mm, respectively. The position is starting from the edge of the black part of the sample. (c) Average reflection, R , and transmission, T , data (averaged over a wavelength range of 500 – 900 nm) as a function of position. The red line indicates the as-deposited boundary between the black and yellow regions, and the black line represents the position for the new boundary at the time of measurements. (d) Optical band gap energy as a function of position. Note that the above optical data representing position 40 mm was obtained from the transformed region.

The position starts from the edge of the black part of the sample. As can be seen, for the black film (position 10 mm), the transmission was close to zero and the absorption was almost wavelength independent in the measured range of 250 – 950 nm and was found to be $\sim 86\%$. In contrast, for the yellow part of the sample (position 70 mm), the transmission spectrum shows characteristic thin film oscillations and an absorption edge at a wavelength of ~ 480 nm, which are consistent with previous results [5, 8]. The absorption spectrum also indicates that light below ~ 400 nm was strongly absorbed. Average reflection, R , and transmission, T , results (averaged over a wavelength range of 500 – 900 nm) are plotted as a function of position in Fig. 3(c). The average transmission increased substantially when the oxygen concentration exceeded the threshold level at positions near 40 mm, while the average reflection remained almost unchanged. In the transformed region (position 40 mm), the transmission and absorption spectra differed noticeably from those for the as-deposited yellow film (position 70 mm). Firstly, the transparency was slightly lower while the absorption was higher. Secondly, there was a small shift of the absorption edge towards higher wavelengths, which is an indication of change in the optical band gap energy [8]. The band gap energy can be determined by employing the Tauc plot method as reported previously [13]. As shown in Fig. 3(d), the band gap energy was found to increase gradually from ~ 2.83 to 2.93 eV when the measurement position was moved from 40 to 70 mm with a spacing of 5 mm. In contrast, the band gap was not developed in the black part of the sample (positions 10 – 30 mm). Note that the high band gap region corresponds to high oxygen content according to ERDA results. Hence, the band gap widening can be attributed to an increase in the oxygen concentration.

Fig. 4(a) shows the change in absorption spectra for the same

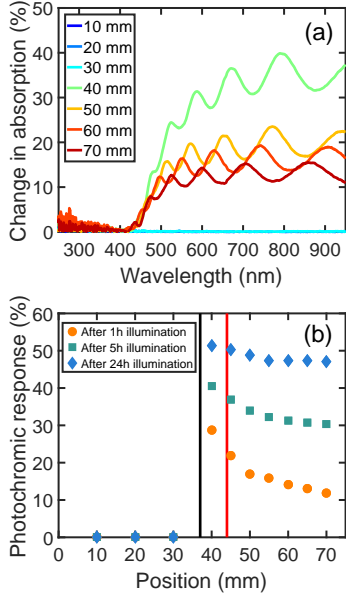


Figure 4: (a) The change in absorption spectra at measurement positions 10 – 70 mm in a YHO thin film sample acquired after one hour light illumination. (b) The photochromic response, as measured by the modulation in the optical transmission before and after light exposure, is plotted as a function of position. The optical transmission was recorded after 1, 5 and 24 h of light illumination, respectively.

YHO thin film sample before and after one hour light illumination. As expected, no change in the absorption in the black part of the sample (positions 10 – 30 mm) was observed. However, in the as-deposited yellow transparent region (positions 50 – 70 mm), the absorption change was diminished as the oxygen concentration was increased in the sample. Notably, the largest increase in light absorption was achieved in the transformed region (position 40 mm). Fig. 4(b) shows the effect of changes in chemical composition on the optical transmission in the photodarkened state. Here, the strength of the photochromic response is defined as the modulation in the optical transmission (averaged over a wavelength range of 500 – 900 nm) acquired before and after light exposure, i.e., $T(\text{before}) - T(\text{after})$. The transmission data was recorded after 1, 5 and 24 h of light illumination, respectively. The most remarkable finding is that the photochromic response was strongest in the transformed region as compared to the rest of the yellow film, in which the photochromic response was decreased gradually from $\sim 30\%$ at position 40 mm to 10% at position 70 mm upon illumination for 1 h. Interestingly, as the illumination time was increased to 5 h, the difference in the photochromic response across the yellow region became less prominent. When the sample was illuminated for 24 h, the difference was further diminished to only a few percent. Overall, the photochromic response increased in a logarithmic fashion with increasing illumination time within the measurement period.

The exact physical mechanism underlying the enhanced photochromism observed in the transformed region is currently elusive. One could speculate that this enhancement might arise from an improved chemical composition in the transformed re-

gion, in which the resulting yellow transparent film is formed by a natural ordering or redistribution of oxygen and hydrogen atoms in the lattice upon an oxidation process. Consequently, an optical band gap is developed at this critical composition. The narrow band gap found in the transformed region leads to increased light absorption mainly in the visible and near-infrared parts of the spectrum in the photodarkened state, eventually contributing to enhance the photochromic reaction.

The present findings might be interesting for potential photochromic devices such as optical memory[14] and sensors [15], in which a maximum achievable photochromic response signal is essential. For device applications, however, YHO thin films with a uniform composition are often required, which can be realized by employing dynamic reactive sputtering deposition [16]. By carefully tuning the deposition conditions, we believe it is feasible to produce uniform black opaque YHO thin films with an oxygen concentration close to a threshold level, e.g., $[O]/[Y]$ at $\sim 0.4 - 0.5$ as suggested by ERDA results. Such black opaque films are expected to switch completely to yellow transparent by annealing at room or elevated temperatures in an oxygen-rich atmosphere, resulting in more stable films with enhanced photochromic effect.

4. Conclusions

We have used reactive magnetron sputtering deposition to fabricate oxygen-containing yttrium hydride thin films with a lateral composition gradient, which allowed us to systematically investigate the effect of changes in oxygen and hydrogen concentrations on their optical properties. The present approach of making films with composition gradient should in principle be suitable for other closely related metal hydride thin film systems as well. We have shown that an as-deposited black opaque oxygen-containing yttrium hydride film can be gradually transformed to a photochromic yellow transparent material when its oxygen concentration exceeded a threshold level by annealing in an oxygen-rich atmosphere. We found that the black to yellow color transformation rate was controlled by the annealing temperature and ambient conditions. In addition, the optical band gap was found to increase with increasing oxygen concentration in the film and was accompanied with a decrease in the photochromic response due to reduced light absorption. The resulting yellow transparent material in the transformed region, with smallest band gap, showed best photochromic performance with enhanced photodarkening reaction.

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References

- [1] J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D. de Groot, N.J. Koeman, Yttrium and lanthanum hydride films with switchable optical properties, *Nature* 380 (1996) 231–234.
- [2] K. Yoshimura, C. Langhammer, B. Dam, Metal hydrides for smart window and sensor applications, *MRS Bull.* 38 (2013) 495–503.
- [3] A.F.T. Hoekstra, A.S. Roy, T.F. Rosenbaum, R. Griessen, R.J. Wijngaarden, N.J. Koeman, Light-induced metal-insulator transition in a switchable mirror, *Phys. Rev. Lett.* 86 (2001) 5349–5352.
- [4] A. Ohmura, A. Machida, T. Watanuki, K. Aoki, S. Nakano, K. Takemura, Photochromism in yttrium hydride, *Appl. Phys. Lett.* 91 (2007) 151904.
- [5] T. Mongstad, C. Platzer-Björkman, J.P. Maehlen, L.P.A. Mooij, Y. Pivak, B. Dam, E.S. Marstein, B.C. Hauback, and S.Z. Karazhanov, A new thin film photochromic material: Oxygen-containing yttrium hydride, *Sol. Energy Mater. Sol. Cells.* 95 (2011) 3596–3599.
- [6] C.V. Chandran, H. Schreuders, B. Dam, J.W.G. Janssen, J. Bart, A.P.M. Kentgens, and P.J.M. Van Bentum, Solid-state NMR studies of the photochromic effects of thin films of oxygen-containing yttrium hydride, *J. Phys. Chem. C.* 118 (2014) 22935–22942.
- [7] T. Mongstad, C. Platzer-Björkman, J.P. Mæhlen, B.C. Hauback, S.Z. Karazhanov, F. Cousin, Surface oxide on thin films of yttrium hydride studied by neutron reflectometry, *Appl. Phys. Lett.* 100 (2012) 191604.
- [8] C.C. You, T. Mongstad, J.P. Maehlen, S. Karazhanov, Engineering of the band gap and optical properties of thin films of yttrium hydride, *Appl. Phys. Lett.* 105 (2014) 31910.
- [9] D. Moldarev, D. Primetzhofer, C.C. You, S.Z. Karazhanov, J. Montero, F. Martinsen, T. Mongstad, B.C. Hauback, E.S. Marstein, M. Wolff, submitted to *Sol. Energy Mater. Sol. Cells* (2016).
- [10] M. S. Janson, CONTES Conversion of Time-Energy Spectra a program for ERDA data analysis, Internal report, Uppsala University, 2004.
- [11] W. A. Lanford, H. P. Trautvetter, J. F. Ziegler, and J. Keller, New precision technique for measuring the concentration versus depth of hydrogen in solids, *Appl. Phys. Lett.* 28 (1976) 566.
- [12] A. Miniotas, B. Hjörvarsson, L. Douysset, P. Nostell, Gigantic resistivity and band gap changes in GdO_yH_x thin films, *Appl. Phys. Lett.* 76 (2000) 2056–2058.
- [13] T. Mongstad, C. Platzer-Björkman, S.Z. Karazhanov, A. Holt, J.P. Maehlen, B.C. Hauback, Transparent yttrium hydride thin films prepared by reactive sputtering, *J. Alloys Compd.* 509 (2011) S812–S816.
- [14] V.A. Barachevsky, Y.P. Stokach, Y.A. Puankov, M.M. Krayushkin, Thermally irreversible organic photochromic compounds for optical memory, *J. Phys. Org. Chem.* 20 (2007) 1007–1020.
- [15] Y. Huang, F. Li, C. Ye, M. Qin, W. Ran, Y. Song, A photochromic sensor microchip for high-performance multiplex metal ions detection, *Sci. Rep.* 5 (2015) 9724.
- [16] C.C. You, T. Mongstad, J.P. Maehlen, S. Karazhanov, Dynamic reactive sputtering of photochromic yttrium hydride thin films, *Sol. Energy Mater. Sol. Cells.* 143 (2015) 623–626.