



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



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## ARTICLE INFO

### Keywords:

Photochromism  
Yttrium hydride  
Chromogenic materials  
Oxidation  
Reactive sputtering deposition  
Optical properties

## 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 ~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.

## 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 [3–6]. 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 tempera-

ture 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 at% 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, photo-

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chromism 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 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 76×26 mm<sup>2</sup>. 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:H<sub>2</sub> 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 ~5 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<sup>2</sup> 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  $^{15}\text{N}$  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  $10^6 \Omega\text{cm}$  in the yellow transparent region. The transformation of the black opaque film adjacent to 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 ~6.5 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 ~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 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. 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 ~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

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