Photochromism in Isotopically Labeled Oxygen-Containing Yttrium—Hydride and Deuteride Thin-Film Systems

Marcos V. Moro, * Sigurbjörn M. Aðalsteinsson, Dmitrii Moldarev, Max Wolff, and Daniel Primetzhofer

Photochromic mono- and bilayered thin films of oxygen-containing isotope-labeled yttrium—hydride (i.e., protium and deuterium) are synthesized via reactive Ar sputtering. Selected samples are encapsulated with transparent diffusion barriers. Combining depth-resolved nondestructive ion beam-based techniques for composition and optical spectrophotometry, material mobility in the samples during illumination and over time is investigated. The results reveal that deuteride thin films exhibit a strong photochromic response equivalent to hydrogenated systems. No evidence of long-distance light-induced hydrogen mobility or thermal diffusion is found. The findings thus show that photochromism is not connected to long-distance material transport. The observations for encapsulated samples also exclude direct material exchange with the environment and any environmental influence on material mobility.

1. Introduction

Oxygen-containing metal—hydride thin films (MEHO, ME = Sc, Y, Nd, Gd, Dy, and Er) are known to be capable of a reversible, color-neutral change in optical transmission in the visible range when illuminated with photons of energies larger than the bandgap of the material, that is, starting from the near-UV part of the visible spectrum.[1–3] This optical response, referred to as photochromism, makes these material systems attractive for potential technological applications in, for example, smart sensors and self-regulating smart-window coatings.[4]

The vast majority of the photochromic MEHO coatings reported have been produced by reactive Ar magnetron sputtering of metallic rare earths in an Ar:H2 environment, followed by oxidation of the films when exposed to air.[5,6] The structure of the resulting films is face-centered cubic (FCC) both before and after oxygen incorporation.[7,8] Several studies[9–11] show that the photochromic response, that is, the relative contrast of the film before and after illumination, as well as the film bandgap, is tunable via the oxygen content in the film. Generally, samples exhibit reversible darkening under illumination (photodarkening) for oxygen-to-metal ratios between 0.45 and 1.5. To obtain knowledge of the chemical formation and oxidation processes, photochromic YHO thin films have been synthesized by reactive electron beam evaporation of metallic yttrium in H2 atmosphere, followed by controlled in situ oxidation and characterization of optical and chemical properties.[12]

The underlying physical and chemical mechanisms of reversible photochromism in MEHO are, however, still a matter of intense debate in the scientific community. Baba et al.[13,14] suggested that the photochromic effect of YHO is connected to photon-induced oxygen diffusion and exchange with the environment. Later, the same group of authors carried out experiments of photochromic YHO at low temperatures (5 K) and concluded that simple anion diffusion in and out of the sample cannot explain the observed changes in optical properties.[15] By in situ analysis of the chemical composition during photodarkening of YHO samples in a high-vacuum environment, it was shown that the oxygen inventory of the films remains indeed unchanged, at least down to levels below 1 at.%.[16] Moreover, we have demonstrated that films isolated from the environment by thin, transparent, and inorganic diffusion barriers still exhibited stable photochromic properties.[17] However, in another more recent work,[18] it was shown that the photochromic effect may depend on the gas environment of the sample and specifically the bleaching kinetics may be strongly affected. In this study, it was shown that films release hydrogen during the initial darkening process, which might be replaced by oxygen from the environment. Dam and co-workers[19–21] suggested that the photon-induced anion O/H mobility to pre-existing vacancies leads to structural rearrangements in the film lattice, which, in turn, is related to the photochromic response. In a recent work,[22] we used results from transmission electron microscopy, X-ray diffraction, and atom probe tomography of GdHO thin...
films, demonstrating phase coexistence of Gd₂O₃ and GdH₂, the latter of which is known to show photochromic properties at elevated pressures with the magnitude of the effect strongly depending on composition.[21,24] Indeed, we could show significant compressive residual stress (≈ 6 GPa) in the films, which could provide an explanation for the optical properties, including short-range anion transport. Recently performed time-dependent density functional theory[25] studies support the hypotheses based on anion transport, as outlined in the aforementioned experimental works.[19–22]

In the present work, we study material diffusion in photochromic films using isotopic labeling to further reveal the role of potentially mobile hydrogen for the photochromic effect. Our results reveal that deuteride thin films are photochromic, while no evidence of long-distance light-induced hydrogen mobility or thermal diffusion was detected.

2. Experimental Section

2.1. Sample Preparation

Photochromic monolayer (YHO and YDO) and bilayer (YHO/YDO) samples were grown by sequential reactive Ar magnetron sputtering, using a compact Balzers Union Sputtering device at Uppsala University. The films were deposited at room temperature on soda-lime microscope glasses (10 × 10 mm² and 1 mm thick), after cleaning with isopropanol (99.9%) in an ultrasonic bath for 5 min. First, two glass substrates were placed into the growth chamber (base pressure < 5 × 10⁻³ Pa) and a single layer of YDₓ was synthesized in Ar:D₂ atmosphere (Ar:D₂ ≈ 0.04) using a high-purity (99.99%) yttrium target. The deposition pressure was 0.6 Pa, and the plasma current was kept constant at 120 mA during 400 s of deposition. To avoid potential contaminations in the deuteride film (especially from hydrogen), the sputtering system was pumped for several hours prior to the first deposition and flushed with Ar gas followed by D₂ gas. After the YDₓ deposition, the samples are oxidized in air by venting of the vacuum chamber. During oxidation, the material changed its color from metallic/opaque to a more transparent (and photochromic) appearance. At this stage, one of the YDO/glass samples remained in the chamber, whereas the other one was replaced by two new substrates. The synthesis process including oxidation was again repeated under the same conditions, except for the reactive gas, which was now H₂ instead of D₂. To avoid target poisoning by the extensive use of different gases, different targets were adopted for each of the reactive gases. In total, three samples were produced: YDO/glass, YHO/glass, and YHO/YDO/glass. Photographs and further descriptions of the samples can be found in other studies.[26,27]

Finally, all samples were simultaneously encapsulated with Al₂O₃ to isolate the films from the environment. The Al₂O₃ layer was deposited in the same sputtering system using Al target (99.999% nominal purity) and Ar sputtering plasma with current of 45 mA. Three 200 s sputtering cycles were performed, each one followed by abrupt oxidation in air. Every sputtering cycle yielded a thin layer of metallic aluminum, and the subsequent oxidation transformed the layer into fully transparent and pinhole-free Al₂O₃. More details on the film synthesis and encapsulation of the samples can be found in the study by Ådalsteinsson et al.[26] In addition, to further investigate a potential exchange of material with the environment or an influence of the environment on migration inside the material, we have also grown two more photochromic samples (YDO/glass and YHO/YDO/glass), but no Al₂O₃ layer was deposited. Both growths were carried out under identical conditions as described earlier.

2.2. Chemical Composition Analysis

Quantitative chemical compositional analysis of the samples was determined on the day of growth by means of nondestructive ion beam-based techniques (IBA). The measurements were carried out at the 5-MV NEC-5SDH-2 Tandem accelerator at Uppsala University.[28] Specifically, Rutherford backscattering spectrometry (RBS) and time-of-flight/energy elastic recoil detection analysis (ToF-E ERDA) techniques were adopted, deploying 2 MeV He⁺ and 36 MeV I²⁺ as impinging projectiles, respectively. The recorded spectra (not shown) were analyzed using a self-consistent and iterative approach.[29] The resulting mass-resolved depth profiles of the samples are shown in Figure 1. Panels (a), (b), and (c) depict the depth profile (in at.%) for Al₂O₃/YDO/glass, Al₂O₃/YHO/glass, and Al₂O₃/YHO/YDO/glass, respectively. The solid lines represent the major chemical elements H, D, O, Al, and Y, whereas light dashed gray lines represent the sum of Na, Si, and Ca from the soda-lime glass substrate. Vertical dashed lines were visual guides delimiting the interfaces between the films. Note that for the Al₂O₃/YDO/glass sample (panel (a)), ≈4 at% of hydrogen was found in the film due to contamination in the sputtering system and in the target (quantification limit < 1 at%). The yttrium concentration was constant throughout the layers.

The thicknesses of the samples (in nm), assuming bulk densities—see supplemental in the study by Moldarev et al.[30]—as well as the averaged bulk [O]/[Y] ratio are summarized in Table 1. The statistical uncertainties on the chemical stoichiometry of elements of O mass and above were estimated to be ≈1 at%, while the depth resolution of the ion beam analysis (IBA) methods was found to be ≈30 nm. For the light species (H and D), systematic uncertainties, potentially arising from the detector efficiency of the ToF telescope deviating from unity and from the specific energy loss of primary ions and recoils, were estimated to be within 15–20% of the deduced isotopic concentrations.[31] However, this systematic uncertainty was minimized in any intercomparison of samples within the same batch (for a more detailed discussion using equivalent samples, see the study by Moro et al.[16]). Note that the precision, which is relevant for comparing measurements on different samples with identical constituents, is much higher (≈1%).

2.3. Optical Analysis

Optical characterization was carried out one day after film growth. During this interval, the samples were kept in air. Optical transmission measurements were done using a Perkin Elmer Lambda 35 UV/Vis spectrophotometer equipped with tungsten–halogen and deuterium light sources. The equipment was set in scan mode, with wavelength in the range of
and scanned at a speed of 240 nm min⁻¹, using a 2 mm-wide slit. All data were normalized with respect to the transmission of air, measured prior to the measurements with photochromic films.

Initially, the optical transmission spectrum of each sample was recorded in the bleached state (i.e., before illumination, transparent stage). Subsequently, the samples were photodarkened using a blue light emission diode (LED) array (400 nm, 75 mW cm⁻²) for 20 min, and another transmission spectrum was recorded in the photodarkened state. We define the photochromic response (i.e., the contrast level) as the difference of the optical transmission (averaged within 500–900 nm) before and after photodarkening with respect to the transmission prior to illumination. All samples relaxed to their initial transmission after ≈3 h when the illumination was stopped.

### 3. Results and Discussion

Figure 2 depicts the optical transmission spectra for all samples before (dashed lines) and after illumination (solid lines). The observed oscillations in transmitted intensity are a consequence of interference; due to the aforementioned averaging, they will have virtually no impact on the quantification of the photochromic response. Optical transmission data of pure glass (gray solid line) and the capping layer deposited onto glass (gray dashed line) are also shown for comparison. As shown in Figure 2, all samples, irrespective of the employed hydrogen isotopes, exhibited a photochromic response: ≈9% for the deuteride (Al₂O₃/YDO/glass), ≈7% for the hydride (Al₂O₃/YHO/glass), and ≈20% for the bilayered (Al₂O₃/YHO/YDO/glass) samples. These values are summarized in Table 1. Total uncertainties of this measurements are estimated to be around 2%.

### Table 1. Summary of film (and capping) thicknesses, bulk composition (i.e., the [O]/[Y] ratio), and their respective photochromic response (in %). See text for more details.

<table>
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<th>Al₂O₃-protected photochromic samples</th>
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<tr>
<td>Cap thickness [nm]</td>
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### Figure 1. Composition depth profiles of the encapsulated oxygen-containing yttrium hydride/deuteride. a) Al₂O₃/YDO/glass, b) Al₂O₃/YHO/glass, and c) Al₂O₃/YHO/YDO/glass. The letters correspond to the different chemical elements and isotopes, represented by the solid lines. Vertical dashed lines indicate film interfaces.

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A first prominent result from our study is that oxygen-containing deuteride films show a photochromic response very similar to their hydrogenated counterparts. To the best of our knowledge, photochromism is unprecedented for a deuterated system. Note in this context that diffusion coefficients are expected to be significantly different for the two isotopes of hydrogen employed. Despite the fact that both deuteride and hydride films were synthesized under similar conditions, the deuterated film shows slightly stronger photochromic response than the hydrogenated one. It is known that oxygen replaces hydrogen during oxidation and the oxygen-to-metal concentration plays an important role for photochromism. The data shown in Figure 1 panels (a) and (b) suggest that deuterated films oxidize slower, which may explain the stronger photochromic effect. This result is consistent with earlier studies,\cite{10} showing that higher oxygen content results in weaker photochromic response. Moreover, the slower oxidation of the D layer might also be related to slower outgassing of D in comparison with H.

Figure 2. Optical transmission as a function of wavelength for the capped YDO (red lines), capped YHO (green lines), and capped bilayered YHO/YHO (blue lines) films, recorded before (dashed lines) and after (solid lines) illumination. For comparison, reference measurements on pure glass (black solid line) and capping layer deposited on glass (black dashed line) are shown.

Figure 3. Chemical depth profile of the Al2O3-protected bilayered samples obtained in the same day of growth (dashed lines) and 9 days after growth (solid lines). Vertical lines indicate film interfaces.
again due to differences in diffusion coefficients; however, further investigation on hydrogen (protium and deuterium) outgassing in YH
prior oxidation is desired for quantitative conclusions.

To investigate mobility and solubility of hydrogen, we analyzed the time evolution of the composition depth profile of the encapsulated bilayered Al
YHO/YDO/glass sample. The results are shown in Figure 3: depth profile of the bilayered Al
YHO/YDO/glass sample at the day of fabrication (without undergoing any photodarkening/bleaching cycle, dashed lines) and after 9 days (undergoing x photodarkening/bleaching cycles, solid lines). We find no exchange or redistribution of hydrogen and deuterium in the two films, indicating low mobility of both protium and deuterium within the layers. This finding shows that photochromism cannot be related to transport of hydrogen over larger distances in the material. Note, in this context, that the depth resolution of the depth profiles is estimated to be around 25 nm, close to the surface with deteriorating resolution at larger depths. The limitations are mainly due to energy straggling and detection resolution. This limited depth resolution will, even for perfectly stacked systems, create an impression that the composition profiles of the individual elements extend beyond the boundaries between the film/layers interfaces, even if this would not be the case. Nonetheless, this effect does not influence the time evolution of the depth profiles of the film constituents, as discussed in detail.

As a complement, we have also measured composition depth profiles for the uncoated samples. Figure 4, panel (a) and (b), shows composition depth profiles for the as-deposited samples and after 9 days of deuteride (YDO/glass) and a bilayered (YHO/YDO/glass) sample, respectively. Again, no redistribution or exchange of hydrogen and deuterium is found. Note that this unprotected bilayered sample, kept in identical conditions as the other samples, went through several illumination cycles. We observe a slight increase in oxygen in both samples, as expected for continuous oxidation of the films and in line with previous observations. These results further prove that hydrogen exchange in or out of the film is not responsible for photochromism.

4. Conclusion

We synthesized mono- and bilayered thin films of oxygen-containing isotope-labeled yttrium–hydride (i.e., protium and deuterium) onto glass substrates by reactive Ar magnetron sputtering and oxidation in air. Chemical depth profiles, deduced by a combination of different ion beam-based techniques, revealed that despite protium and deuterium films were grown under similar conditions; their averaged bulk chemical stoichiometry is different, suggesting that the oxidation process progresses slower in the deuterium than protium film. Optical transmission spectrophotometer analysis, carried out one day after fabrication, revealed that all samples are photochromic. When cycling the darkening and bleaching process, neither detectable interdiffusion within the layers, nor material exchange with the environment, was observed for a time span of up to 9 days. These results further support earlier proposals of the photochromic effect being likely related to either short-distance hydrogen transfer at the boundaries of coexisting phases or lattice rearrangements.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
deuterium, diffusion barriers, isotopic labeling, material migration, oxygen-containing yttrium hydride, photochromism

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