Photochromic Response of Encapsulated Oxygen-Containing Yttrium Hydride Thin Films

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Photochromic oxygen-containing yttrium-hydride thin films are synthesized by argon magnetron sputtering on microscope slides. Some of them are encapsulated with a thin, transparent, and nonphotochromic diffusion-barrier layer of either Al2O3 or Si3N4. Ion-beam-based methods prove that these protective diffusion barriers are stable and free from pinholes, with thicknesses of only a few tens of nanometers. Optical spectrophotometry reveals that the photochromic response and relaxation time for both protected and unprotected samples are almost identical. Ageing effects in the unprotected films lead to degradation of the photochromic performance (self-delamination), whereas the photochromic response for the encapsulated films is stable. The results show that the environment does not play a decisive role for the photochromic process and the encapsulation of oxygen-containing rare-earth hydride films with transparent and nonorganic thin diffusion-barrier layers provides long-time stability of the films, mandatory for applications as photochromic coatings on, e.g., smart windows.

1. Introduction

Recently, it was found that oxygen-containing rare-earth metal hydride thin films (REHO) change their optical transmission under illumination with visible light at ambient conditions.[11–13] In situ composition analysis of photochromic oxygen-containing yttrium hydride (YHO, RE = Y) samples under illumination showed that photodarkening can be triggered in high-vacuum conditions (base pressure ~10⁻⁷ Pa) and is not related to significant chemical composition changes (~1 at%) of the films.[14] These results suggest that the photochromic properties are rather linked to, e.g., changes in the structure or electronic rearrangements. The exact stoichiometry, structures, and phases of possible photochromic systems in both thin films and bulk, are, however, still a matter of scientific debate.[14,12,13,16] In a recent work,[17] we have—for photochromic GdHO thin films—observed a columnar-type structure and a coexistence of fcc REH₂-like and bixbyite-like RE₂(H₃O)₂ phases with compressive residual stress of the order of gigapascals in the films. As it is known that yttrium hydride is photochromic at high pressures,[18] we propose a similar mechanism of photodarkening in REHO, accompanied by a photon-induced hydrogen transfer from the bixbyite RE₂O₃ phase into the fcc REH₂ phase. Recent calculations using time-dependent density functional theory based on excited-state molecular dynamics support this hypothesis.[19] In parallel, a possible gas exchange between the film and the environment has been suggested as the key mechanism to the photochromic response.[19] However, a close look at the data presented by the authors[20,21] shows that a change of the relative intensity of the overlapping Bragg peaks of the two phases induced by material transport from one to another can provide...
an alternative explanation. Later, the same group of authors suggested—based on photodarkening results obtained at low temperatures (5 K)—that a simple anion transfer out of the film cannot be responsible for the photochromic process.[12]

Herein, we show that encapsulated photochromic REHO films with transparent, nonphotochromic, and thin diffusion barriers perform equally well as uncapped films. Moreover, we prove that the films sealed against the environment are still photochromic and long-time stable as oxidation is inhibited by the diffusion barrier. Our results unambiguously demonstrate that material transport in and out of the film cannot be the reason for the photochromic effect.

2. Experimental Section

Two batches of two YH_{2} samples each (total four samples) were reactively grown by Ar-magnetron sputtering onto soda-lime glass substrates (ultrasonically cleaned microscope slides, 10 × 10 mm\(^{2}\) and 1 mm thick) using a compact Balzers Union sputtering device. Further details on the synthesis of REHO can be found elsewhere.[23] After the metal-hydride deposition, the samples were exposed to air for oxidation. At this stage, the films changed their appearance from opaque to (photochromic) yellowish transparent. After exposure to air, one sample was kept in air, and the other was capped with either a thin layer of Al_{2}O_{3} or Si_{3}N_{4} (≈20 min of time lag). Both these layers have good antireflective properties, lower absorption of visible light in comparison to YHO. The optical bandgap (\(E_{g}\)) of amorphous Al_{2}O_{3} and Si_{3}N_{4} is \(E_{g} \approx 5–7\) eV[24–25] and \(E_{g} \approx 2.7\) eV[12] for YHO. The fabrication processes are well established (with low contamination levels) and used in semiconductors and solar cells as diffusion-barrier coatings.[26–29]

The Al_{2}O_{3} capping layer was deposited in a pure Ar environment (base pressure ≈10^{-10} Pa). During deposition, the Ar pressure was maintained at ≈5 Pa. The target–substrate distance was 5 cm and the plasma sputtering current 45 mA. Three 200 s sputtering cycles were performed, each one followed by an abrupt oxidation by air. Every sputtering cycle yielded a thin layer of metallic aluminum, and the subsequent oxidation transformed the layer into fully transparent Al_{2}O_{3}. For the Si_{3}N_{4} capping layer, one sample was transferred to a reactive magnetron sputtering system (Von Ardenne CS 730S at MyFab, Uppsala University) equipped with a silicon target (nominal purity >99.999%). The Ar:N_{2} ratio was kept at 20:40 sccm with 500 W of plasma power (base pressure during growth ≈0.8 Pa). The resulting deposition rate was ≈3 Å s\(^{-1}\).

The chemical composition of the samples was obtained by combining results from four ion-beam-based methods: Rutherford backscattering spectrometry (RBS), time-of-flight elastic recoil detection analysis (ToF-E ERDA), nuclear reaction analysis (NRA), and elastic backscattering spectrometry (EBS). All measurements were conducted at the 5-MV NEC-5SDH-2 tandem accelerator (Tandem laboratory, Uppsala University).[30] The spectra were analyzed following an iterative approach (see Moro et al.[33] for further details on the techniques and evaluation procedure), providing composition depth profiles of the samples, including quantification of trace impurities.

In Figure 1, the chemical composition depth profiles from the ToF-E ERDA analysis are shown. Panels (a) and (b) show the results from the first batch of twin YHO samples, one being encapsulated with an Al_{2}O_{3} layer. Panels (c) and (d) represent depth profiles from the second batch, i.e., the uncapped and Si_{3}N_{4}-capped films, respectively. The chemical composition of the YHO of each batch of samples was identical within ±2 at% (depth range to ≈480 nm due to limited probing depth of ToF-ERDA). Note that the ToF-E ERDA depth profiles contain inputs from other methods (see, e.g., Adalsteinsson et al.[3] for a similar system). Light impurities (C and F) originating from the deposition process were found for all samples (in sum ≤5–7 at%). The encapsulation did not affect the chemical composition of the films and the average [O]/[Y] ratio in the YHO bulk was found to be ≈0.51 (for Al_{2}O_{3} batch) and ≈0.43 (for Si_{3}N_{4} batch, in agreement with the composition range showing photochromism 0.40 ≤ [O]/[Y] ≤ 1.5).[12] From the RBS results (not shown), the total film thicknesses (assuming YHO bulk densities—see supplemental information in Moldarev et al.[13]) were found to be 412 and 478 nm for the Al_{2}O_{3} and Si_{3}N_{4} batches, respectively. Moreover, RBS analysis did not reveal any presence of yttrium on the encapsulated sample surface (less than 1 at%), indicating the absence of holes and cracks in the capping layers. The signal of Y, O, and H found in the capping layers in Figure 1 is a consequence of the depth resolution of the ToF-E ERDA as well as multiple scattering effects (the latter especially for Y). The thicknesses, extracted from the RBS data, of the capping layers are 52 and 60 nm for Al_{2}O_{3} and Si_{3}N_{4}, respectively. Film thicknesses and their chemical compositions are summarized in Table 1.

Optical measurements were conducted using a Perkin Elmer Lambda 35 UV–vis spectrophotometer equipped with a tungsten halogen and deuterium light source. The optical transmission was calibrated with respect to the transmission of air. Optical scans were done in the wavelength range of [300–1000] nm, at 240 nm min\(^{-1}\) ( slit size of 2 nm). First, the optical transmission was measured while the samples were fully bleached (i.e., initial stage before illumination), followed by a measurement after the samples were photodarkened for 20 min using an LED array of blue light (wavelength 400 nm and intensity ≈10 mW cm\(^{-2}\)). The photochromic response is defined as the ratio of the averaged optical transmission before and after illumination (integrated in the wavelength range [500–900] nm). All samples relaxed to their initial transmission once illumination was stopped. To eliminate the effect of different absorption coefficients in the capping layers, all samples were illuminated through the glass substrate. A potential influence from reflection at the interfaces is negligible.

3. Results and Discussion

In Figure 2a,b, the optical transmission spectra of the YHO samples before (dashed lines) and after (solid lines) illumination are shown. The measurements were conducted ≈6 h after fabrication. For comparison, spectra from pure glass (black solid lines) and the capping layers deposited onto glass (black dashed lines) are shown. The photochromic responses are ≈18% and ≈15%, for the uncovered (blue lines) and Al_{2}O_{3}-encapsulated YHO (red lines) samples, respectively. For the second batch, a
generally higher photochromic response, \(\approx 33\%\) and \(\approx 36\%\), was found for the uncovered (blue lines) and \(\text{Si}_3\text{N}_4\)-encapsulated (red lines) YHO samples, respectively. It turns out that encapsulation does not influence the photodarkening of the films.

The bleaching process, i.e., the relaxation from the photodarkened to the original and transparent stage, showed similar relaxation time constants to the initial transmission (deduced from exponential fits to the time-dependent optical transmission data) of 18.5 min (as-deposited) and 19.3 min (encapsulated) for YHO and from the \(\text{Al}_2\text{O}_3\) batch, and 46.1 min (as-deposited) and 46.4 min (encapsulated) for YHO films from the \(\text{Si}_3\text{N}_4\) batch, respectively. Note that any possible systematic uncertainty in time constants arising from the time span required by the spectrophotometer to record a full transmission spectrum is reduced in an intercomparison of samples measured under the same experimental conditions. A summary of the photochromic properties is given in Table 1. As the \(\text{Si}_3\text{N}_4\) capping layer is a stable and oxygen-free diffusion barrier, we can exclude any oxygen uptake or release by REHO films during photodarkening and bleaching.

To investigate the aging and degradation of the films, we measured the optical response of the samples from the \(\text{Al}_2\text{O}_3\) batch at several instances up to 14 days after growth. The results are shown in Figure 3a for the encapsulated film and Figure 3b for the unprotected one (transmission spectra recorded in the same way as in Figure 2). The photochromic performance of the protected film remains unchanged, within \(\pm 2\%\)–3\%. For the unprotected YHO film, delamination was observed after a few days of exposure to air, and its optical properties had been degrading even more rapidly. Note that continuous air exposure of uncapped films may initially result in either an increasing or decreasing of the photochromic response as this quantity depends on the oxygen concentration and is largest for \([\text{O}]/[\text{H}] \approx 0.8\).[12] In addition, it has also been observed that the photochromic response of (unprotected) YHO is affected by other factors, e.g., previous darkening/bleaching cycles ("memory effect").[1] Our results show that once capped, the oxygen concentration in the YHO film remains constant, allowing us to tailor design photochromic films with

| Diffusion barrier | \(\text{Al}_2\text{O}_3\) layer | \(\text{Si}_3\text{N}_4\) layer |
|------------------|-----------------|-----------------|
| Cap thickness [nm] | Uncapped | Capped | Uncapped | Capped |
| Film thickness [nm] | 412 | 412 | 478 | 478 |
| Average \([\text{O}]/[\text{Y}]\) ratio (bulk) | 0.51 | 0.50 | 0.45 | 0.44 |
| Photochromic response [%] | 18 | 15 | 33 | 36 |
| Bleaching constant [min] | 18.5 | 19.3 | 46.1 | 46.4 |

**Figure 1.** a,b) Depth profiles deduced by ToF-E ERDA for YHO samples from the first batch: a) uncapped and b) capped with \(\text{Al}_2\text{O}_3\). c,d) Data for the second batch of YHO samples (uncapped (c) and capped with \(\text{Si}_3\text{N}_4\) (d)).

**Table 1.** Summary of the film (and capping) thicknesses and their respective optical properties.

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long-time stability. Thus, to obtain reproducible and maximized photochromic response optimizing the oxidation process before depositing a capping layer, potentially by controlled oxidation,[10] is desirable.

4. Conclusion

We have fabricated photochromic YHO films encapsulated by transparent and nonphotochromic diffusion-barrier layers of Al$_2$O$_3$ and Si$_3$N$_4$. Composition depth profiling shows that the encapsulation layers are stable, free of pinholes or cracks, and only a few tens of nanometers thick. The photochromic properties (photodarkening response and relaxation time) for the encapsulated samples are the same as those of freshly prepared YHO unprotected films but stable over time. From our results, we conclude that material transport to and from the ambient, e.g., release and uptake of oxygen or other species cannot explain the photochromic effect. In addition, our results demonstrate that photochromic films can be efficiently protected against oxidation and become long-time stable, which is a huge step forward toward technological application.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors.

Keywords

diffusion barriers, oxygen-containing yttrium hydride, photochromism

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