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## Photochromism of rare-earth metal-oxy-hydrides

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Recently, thin films of yttrium oxy-hydride  $(YO_xH_y)$  were reported to show an unusual colorneutral photochromic effect promising for application in smart windows. Our present work demonstrates that also oxy-hydrides based on Gd, Dy, and Er have photochromic properties and crystal structures similar to  $YO_xH_y$ . Compared to  $YO_xH_y$ , the optical bandgaps of the lanthanide based oxy-hydrides are smaller while photochromic contrast and kinetics show large variation among different cations. Based on these findings, we propose that cation alloying is a viable pathway to tailor the photochromic properties of oxy-hydride materials. Furthermore, we predict that the oxyhydrides of the other lanthanides are also potentially photochromic. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4995081]

Upon hydrogenation, yttrium shows a metal insulator transition accompanied by dramatic changes in optical and electrical properties.<sup>1</sup> Pd capping of Y thin films allows for a reversible (de)hydrogenation.<sup>2,3</sup> The optical changes involved in the (de)hydrogenation process lead to intriguing findings such as the switchable mirror effect in YH<sub>x</sub>.<sup>2</sup> Depending on the H concentration, the Y-H system exhibits three structural phases. Upon hydrogenation, metallic Y with a hexagonal structure transforms into the cubic dihydride phase  $(\beta$ -YH<sub>1.9-2.1</sub>) and finally the hexagonal trihydride phase  $(\gamma$ -YH<sub>2.7-3</sub>).<sup>1</sup> While the YH<sub>1.9+ $\delta$ </sub> phase is a black and opaque metal, the trihydride is a transparent semiconductor with a direct optical bandgap of 2.6 eV.<sup>5</sup> A unique photochromic effect was recently observed in magnetron sputtered YO<sub>x</sub>H<sub>v</sub> thin films after excitation by an AM1.5 solar spectrum at room temperature and ambient pressure.<sup>6</sup> This polycrystalline semiconductor has an optical bandgap of about 2.6 eV and an fcc crystal structure with a lattice constant of 5.35–5.40 Å.<sup>7,8</sup> The initially transparent material photodarkens in a wide spectral range covering the visible (VIS) and near infrared (NIR) with a time constant in the order of minutes.<sup>6</sup> Hence, YO<sub>x</sub>H<sub>v</sub> is a promising material for application in energy saving smart windows and other chromogenic devices. Most photochromic materials are organic in nature and exhibit narrow spectral absorption bands together with fast switching behavior.<sup>9-11</sup> However, due to limited stability vs. oxygen, humidity, and heat, as well as ultra-violet (UV) irradiation induced fatigue,<sup>11</sup> complex processing is often required to tailor the photochromic response and to enhance the product lifetime. In contrast, inorganic photochromic materials have the potential for higher physico-chemical stability and show much broader absorption bands, resulting in color-neutral photochromism, albeit at lower switching speed. A well-known example of inorganic photochromic materials are silver halide doped glasses where the photochromic effect is based on the reversible formation of plasmonic nanoparticles.<sup>12,13</sup> While the photochromic mechanism in  $YO_xH_y$  remains to be uncovered, Mongstad *et al.* suggested that the fcc crystal structure and the presence of oxygen are essential for the photochromic effect.<sup>6,14</sup>

In this work, we investigate the structural and optical properties of rare-earth metal based oxy-hydrides in comparison to YO<sub>x</sub>H<sub>y</sub>. The lanthanides show physical and chemical behavior very similar to Y in terms of mostly trivalent oxidation state, ionic radius, as well as crystal structure and properties of compounds formed with oxygen and hydrogen. Indeed, we find that the oxy-hydrides of Gd, Dy, and Er are photochromic. This allows us to explore possible structural and chemical effects on the photochromic properties of the MO<sub>x</sub>H<sub>y</sub> material family. Interestingly, we observe (i) lower optical bandgaps of the rare-earth oxy-hydrides compared to YO<sub>x</sub>H<sub>v</sub>, (ii) a large variation of photochromic kinetics for different M, and (iii) exceptionally strong photochromism in GdO<sub>x</sub>H<sub>y</sub> particularly in the NIR spectral region. Moreover, it is demonstrated that the formation of transparent photochromic  $MO_xH_y$  thin films only takes places above a certain critical value of the total pressure during reactive sputter deposition.

A series of yttrium and rare-earth (Gd, Dy, Er) based thin films was prepared on unheated UV-grade fused silica (f-SiO<sub>2</sub>) substrates by reactive direct current magnetron sputtering of 2-inch metal targets (99.9% purity) at 100 W in an Ar/H<sub>2</sub> gas mixture (5N purity) with 12.5 vol. % of H<sub>2</sub>. The deposition system was kept at a base pressure below  $3 \times 10^{-6}$  Pa and the total pressure, *p*, during deposition was varied by means of a butterfly reducing valve mounted at the turbo molecular pump inlet. Structural, optical, and photochromic properties were investigated by a combination of X-ray diffraction (XRD), optical spectroscopy, and UV excitation.

In contrast to what was previously reported by Mongstad *et al.*,<sup>6,7</sup> we do not always obtain transparent and photochromic films after reactive sputtering of Y in  $Ar/H_2$  mixtures followed by exposure to air. Uncapped films prepared below a certain critical deposition pressure remain dark metallic upon exposure to air. These films are not photochromic and show a low transmittance over the entire spectral range, except for a narrow region in red part of the visible spectrum (Fig. 1).

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FIG. 1. Characteristic transmittance window of Y and rare-earth dihydride thin films directly prepared by reactive magnetron sputtering below the critical deposition pressure. The difference in maximum transmittance is a result of film thickness variation between 188 nm (M = Dy) and 320 nm (M = Gd).

Such a transmittance window has been reported previously for Y-La dihydride films by van Gogh et al.--in particular in the hydrogen poor part of the dihydride solid solution (i.e., fcc-YH<sub>19+ $\delta$ </sub>).<sup>5</sup> It arises from a combination of weak free electron and inter-band absorption near the plasma frequency. The position (wavelength) of the dihydride window has been reported to shift with hydrogen/metal ratio<sup>15,16</sup> as well as Y/La ratio in alloyed hydrides.<sup>5</sup> We do not find any systematic correlation of the transmittance window peak wavelength with the cation size or lattice constant. Probably, this variation is an effect of minor changes in the H/M ratio, or rather free electron density, in different samples. Nevertheless, the observation of the characteristic transmittance window is a strong indicator for the presence of the metallic fcc-dihydride phase (MH<sub>2</sub>). In conjunction with the XRD analysis (see below), this demonstrates that stable rareearth dihydride thin films can be produced directly by reactive sputter deposition i.e., without the need for Pd capping and a separate hydrogenation step.

When the Y and lanthanide films are deposited above the critical pressure, initially they also appear black opaque inside the vacuum chamber and in an attached glove box  $(p_{O2} < 1 \text{ ppm})$ . However, upon exposure to air, they rapidly react and become transparent. Our preliminary ion-beam analysis results indicate an oxygen content of 20-30 at. % (not shown), which is comparable to earlier reports on YO<sub>x</sub>H<sub>v</sub>.<sup>6</sup> Therefore, these transparent and photochromic materials are referred to as metal oxy-hydrides  $(MO_xH_y)$ . The uptake of oxygen from air is driven by the large difference in formation enthalpy between oxides and hydrides e.g.,  $-1895 \text{ kJ/mol}^{17}$  for bixbyite-Y<sub>2</sub>O<sub>3</sub> vs.  $-228 \text{ kJ/mol}^{18,19}$ for YH<sub>2</sub>. Probably, the observed deposition pressure dependent oxidation behavior is related to a higher porosity of the as-prepared MH<sub>2</sub> films when grown at higher pressures. The micro-structure of sputtered thin films strongly depends on the ad-atom mobility of deposited species, which is controlled by the flux of energetic particles arriving at the film surface (mainly sputtered atoms and back-reflected Ar neutrals) as well as the substrate temperature. These effects result in the well-known structure-zone-models<sup>20</sup> characteristic of sputtered thin films describing the formation of denser micro-structures at low deposition pressures. This is because of collisions of the energetic particles with the process gas on their way from sputter target to substrate, effectively reducing their average energy as the deposition pressure is increased. These concepts explain qualitatively our observation that a critical deposition pressure,  $p^*$ , exists such that films deposited at  $p < p^*$  remain metallic dihydrides whereas films deposited above  $p^*$  transform into semiconducting oxy-hydrides upon air exposure. Experimentally, we find  $p^*(YO_xH_v) \simeq 0.4 Pa$  whereas  $p^* \simeq 0.6 Pa$  for Gd, Dy, and Er oxy-hydrides. This material dependence of  $p^*$ , and hence MH<sub>2</sub> film density, is likely attributed to a significant contribution of back-reflected Ar neutrals to the overall energy flux towards the growing films. Both the reflection probability and average energy of reflected Ar neutrals increase with atomic mass of the target.<sup>21,22</sup> Taking into account the large mass difference between the lanthanides and Y, it is therefore plausible that a higher gas pressure is required in the case of Gd, Dy, and Er to achieve similar (porous) thin film micro-structure as in YH<sub>x</sub> allowing for airoxidation and formation of MO<sub>x</sub>H<sub>y</sub>.

To investigate the effect of different cations and postdeposition oxidation on the thin film crystal structure, the lattice constants are summarized in Fig. 2. The well-known lanthanide contraction with increasing number of 4f-electrons is reflected in the systematic decrease of lattice constants of the fcc-MH<sub>2</sub> dihydrides (open circles) as well as the cubic bixbyite  $M_2O_3$  oxides<sup>17</sup> (open triangles) with increasing atomic number. Although Y is not a lanthanide, the lattice constant of Y2O3 can be sorted in between Dy and Er. All films sputter deposited at pressures below  $p^*$  (Y at 0.3 Pa and Gd, Dy, and Er at 0.5 Pa) are black metallic upon deposition and remain so when exposed to air. Their diffraction patterns are consistent with the face centered cubic (fcc) structure of the CaF<sub>2</sub> prototype (space group Fm-3 m) characteristic of the metallic  $\beta$ -MH<sub>2</sub> phases. We find a 0.8–1.2% lattice expansion of these directly sputtered dihydride films (full red circles)



FIG. 2. Lattice constants of Yttrium and lanthanide based dihydride  $MH_2$ (red symbols), oxide  $M_2O_3$  (blue symbols), and photochromic  $MO_xH_y$  oxy-hydride (black symbols) thin films. Experimental XRD results of the present work (full symbols) are compared to reference data taken from the ICDD-PDF database (open symbols). Note that due to the structural similarity to the fcc unit cell only 1/2 of the bixbyite  $M_2O_3$  lattice constant is shown here.

relative to the reference values taken from ICDD-PDF (open circles). The lattice constant value of  $5.27 \pm 0.01$  Å of sputtered yttrium hydride is in agreement with an earlier report by Mongstad *et al.*<sup>7</sup> In comparison, we observe significantly smaller lattice constants in Pd capped YH<sub>2</sub>, DyH<sub>2</sub>, and ErH<sub>2</sub> thin films prepared by sputtering of metal layers in pure Ar followed by a separate hydrogenation step at  $p_{H2} = 1$  bar at RT (full red diamonds). These results are closer to the reference values which represent highly ordered structures obtained by hydrogenation of (bulk) metals at elevated temperatures. Since the Pd capped films were grown using the same sputter targets, substrates, pressure, and discharge power, we can rule out target impurities and energetic particle bombardment effects as the origin of the lattice expansion of the *directly sputtered* MH<sub>2</sub> films. Instead, it seems plausible that this effect is related to the interaction of H with the lattice. In contrast to hydrogenation, reactive sputtering can be regarded as a non-equilibrium process. Therefore, a certain amount of disorder of the H sublattice may be present in *directly sputtered* MH<sub>2</sub> films, i.e., a fraction H occupies the octahedral lattice sites, instead of tetrahedral sites as in the ideal fcc-MH<sub>2</sub> structure.

The transparent photochromic oxy-hydride MO<sub>x</sub>H<sub>y</sub> films grown at pressures above  $p^*$  (Y at 0.5 Pa and Gd, Dy, and Er at 0.7 Pa) retain the fcc structure but with a substantial lattice expansion of 1.9–2.8% relative to the corresponding MH<sub>2</sub> films sputtered below  $p^*$ . This lattice expansion is clearly attributed to the incorporation of oxygen after air exposure. We find a value of  $5.38 \pm 0.01$  Å for YO<sub>x</sub>H<sub>y</sub> which is within the range of values reported in earlier publications.<sup>7,8</sup> Remarkably, the MO<sub>x</sub>H<sub>v</sub> lattice constants follow the trend of the lanthanide contraction of the bixbyite-M<sub>2</sub>O<sub>3</sub> compounds (open triangles).<sup>17</sup> Hence, cation substitution allows for tuning of the unit cell dimensions of rare-earth based  $MO_xH_y$ and could thereby enable tailoring of optical and electrical properties. In addition, for each cation M the absolute lattice constant of the MO<sub>x</sub>H<sub>y</sub> is even larger than that of the corresponding structural unit of the bixbyite-M<sub>2</sub>O<sub>3</sub> unit cell. While this effect is puzzling at first, it can be explained by a large concentration of H<sup>-</sup> ions present in the fcc-MO<sub>x</sub>H<sub>v</sub> structure. Considering charge neutrality and attributing formal valencies of  $M^{3+}$  and  $O^{2-}$ , the valence of H in  $MO_xH_v$ can be estimated from the chemical composition data obtained by ion beam analysis (not shown). In fact, we find that charge neutrality is obeyed (within measurement accuracy) only if we assign a valence of -1 to H, whereas assuming H in the form of H<sup>+</sup> or OH<sup>-</sup> would result in violation of the charge neutrality. Interestingly, Miniotas et al. arrived at the same conclusion about the role of H in GdO<sub>x</sub>H<sub>y</sub> thin films.<sup>23</sup> Hence, in a simplified picture, we can regard the expanded fcc-MO<sub>x</sub>H<sub>y</sub> structure as a bixbyite-M<sub>2</sub>O<sub>3</sub> structure where  $O^{2-}$  is substituted by  $H^{-}$  with some additional  $H^{-}$ occupying the structural O vacancies of the bixbyite lattice. Further dedicated experiments are required to directly confirm the presence of H<sup>-</sup> ions in MO<sub>x</sub>H<sub>y</sub> materials.

All the oxy-hydrides we have investigated show photochromic behavior. The changes of spectral transmittance of a set of Y and lanthanide  $MO_xH_y$  thin films due to UV irradiation are compared in Fig. 3(a). Employing the Tauc plot method, we find that  $YO_xH_y$  has a bandgap of  $E_g = (2.60 \pm 0.05)$  eV consistent with earlier reports.<sup>6,7</sup> The lanthanide oxy-hydrides



FIG. 3. Photochromic response of Y and lanthanide oxy-hydride thin films (thickness between 270 and 350 nm) after 5 h of UV illumination at 5070  $\mu$ Wcm<sup>-2</sup>. (a) Transmittance before (solid lines) and after photo-darkening (dotted lines). (b) Corresponding change of absorption coefficient. Note that the absorption coefficients are calculated taking into account the reflectance  $R(\lambda)$  (not shown) using the expression  $T(\lambda) = [1-R(\lambda)] \exp[-\alpha(\lambda)d]$ .<sup>24</sup> The normalized human eye luminosity function according to Sharpe *et al.*<sup>25</sup> is shown as a dashed curve in (b). (c) Photograph of a 500 nm YO<sub>x</sub>H<sub>y</sub> film or glass after UV illumination through shadow masks illustrating the transparent "bleached" state (letters) and two levels of photochromic contrast.

have lower bandgaps of 2.40 eV (ErO<sub>x</sub>H<sub>y</sub>) and 2.25 eV  $(GdO_xH_y \text{ and } DyO_xH_y)$ . This confirms the general notion that the bandgap of the MO<sub>x</sub>H<sub>y</sub> oxy-hydrides is substantially lower than that of the corresponding bixbyite-M<sub>2</sub>O<sub>3</sub> oxides (4.9-5.4 eV).<sup>17,26</sup> Furthermore, the best Tauc fits were obtained with an exponent of 1/2 indicating that the bandgaps of all oxy-hydrides are indirect (see Fig. S3, supplementary material). Using an exponent of 2 in the Tauc plot (assuming a direct bandgap) would result in erroneous band-gap values approximately 1 eV larger than given above. Perhaps the only comparison available is a report by Miniotas et al. stating  $E_g = (3.2 \pm 0.2) \text{ eV}$  for a GdO<sub>0.6</sub>H<sub>1.53</sub> (19 at. % O) thin film.<sup>2</sup> Since the oxygen content is very close to our GdO<sub>x</sub>H<sub>v</sub> material and not all analysis details were disclosed, they very likely overestimated the bandgap value by assuming a direct transition. We did not observe any change of  $E_g$  due to photodarkening. For all MO<sub>x</sub>H<sub>y</sub> films, UV illumination causes a decrease of transmittance in a wide spectral range from  $E_g$  to 2500 nm and beyond. The corresponding difference in the optical absorption coefficient is shown in Fig. 3(b) and allows for a direct comparison of the photochromic effect. A broad maximum of the photochromic response is observed in each material. In the case of  $YO_xH_y$ , this maximum is centered at 550 nm explaining the color-neutral appearance of photodarkening, whereas for M = (Dy, Er), the maxima are redshifted towards the long-wavelength limit of the human eye luminosity function. While in the case of M = (Y, Dy, and Er)the photochromic effect is similar in magnitude ( $\Delta \alpha_{max} \simeq 20\,000 \,\mathrm{cm}^{-1}$ ) and decreases towards the NIR,  $GdO_xH_y$ shows an unusually strong photochromic response extending far into the NIR. This unique effect could be related to a large increase in free-electron absorption during photo-darkening. In fact, the resistivity of  $YO_xH_y$  has been reported to decrease (increase) reversibly along with photo-darkening (bleaching).<sup>6</sup> Further experiments are planned to confirm this hypothesis.

We define the (absolute) photochromic contrast  $\Delta T(\lambda,t)$ as the change of transmittance with respect to the initial value,  $T_0$ , in the bleached state before UV-illumination, i.e.,  $\Delta T(\lambda, t) = T_0(\lambda, 0) - T(\lambda, t)$ . In general, for each material the optical contrast is a function of film thickness and illumination conditions. Thus, in order to compare the photochromic performance of the different oxy-hydride materials, another set of samples of the same thickness (300 nm) have been illuminated under the same conditions followed by bleaching in dark conditions at room temperature. A comparison of the time dependent and spectral averaged contrast,  $\langle \Delta T \rangle$ , is shown in Fig. 4. As expected from Fig. 3(a), YO<sub>x</sub>H<sub>y</sub> is the most transparent material in the bleached state ( $\langle \Delta T_0 \rangle$ ) = 79.8%) while the lanthanide oxy-hydrides are initially less transparent ( $\langle \Delta T_0 \rangle = 67.9 - 71.3\%$ ). These differences are mainly due to the lower bandgap and higher sub-bandgap absorption (Urbach's tail)<sup>27</sup> present in the lanthanide oxyhydrides (see Fig. S3, supplementary material). During photo-darkening, all materials initially show a fast (nearly exponential) increase of contrast followed by a slow change with nearly linear behavior until the light source is switched off after about 8 hours. In particular,  $GdO_xH_y$  and  $YO_xH_y$ show a fast photochromic response and reach large optical contrast values of  $\langle \Delta T \rangle = (25-33)\%$  already after 15 min of illumination. While the maximum optical contrast values of Y, Dy, and Er are comparable  $\langle \Delta T \rangle = (33-37)\%$ , a



FIG. 4. Wavelength averaged optical contrast of Y and lanthanide oxyhydride films (d = 300 nm) during UV illumination at 5860  $\mu$ W cm<sup>-2</sup> followed by (thermal) bleaching in the dark. The spectral averaging between 450 and 1000 nm effectively reduces the influence of optical interference patterns on  $\Delta T$ (t).

significantly higher maximum contrast of  $\langle \Delta T \rangle = 45.5\%$  is observed for Gd. According to Fig. 3(b), this enhanced photochromic contrast is a result of the large absorption coefficient change of GdO<sub>x</sub>H<sub>y</sub> especially in the NIR range. The kinetics of  $\langle \Delta T(t) \rangle$  during bleaching are well described by an exponential decay function  $\langle \Delta T(t) \rangle \propto \exp(-t/\tau_B)$  using the (thermal) bleaching time constant,  $\tau_B$ , as a fitting parameter. We find that DyO<sub>x</sub>H<sub>y</sub> bleaches the fastest ( $\tau_B = 215 \pm 15$  min), followed by Y and Gd, while ErO<sub>x</sub>H<sub>y</sub> shows the slowest bleaching rate of all materials ( $\tau_B = 1260 \pm 80$  min). Our ongoing studies indicate that the bleaching kinetics not only depend on the cation but also on sputter deposition parameters and illumination conditions. Therefore, additional experimentation is required for a more quantitative comparison.

In conclusion, our work demonstrates that (i) stable lanthanide dihydride thin films can be grown directly by reactive magnetron sputtering, (ii) lanthanide oxy-hydride thin films exhibit a photochromic effect similar to YO<sub>x</sub>H<sub>y</sub> suggesting a common physical mechanism, (iii) initial transmittance, photochromic contrast values and photo-darkening speed are promising for applications such as smart windows, (iv) cation alloying is a viable approach to tailor the photochromic properties of MO<sub>x</sub>H<sub>v</sub> because they share the same fcc-structure while optical bandgap, photochromic contrast, and bleaching rate vary substantially between different cations. Based on the presented results, we predict that the oxyhydrides of the remaining rare-earths (incl. Sc) are also potentially photochromic. Systematic synthesis and exploration of their properties might lead to further insight into the physical mechanisms governing the photochromic effect in this class of materials.

See supplementary material for further details regarding XRD analysis, XRD patterns of  $MH_2$  and  $MO_xH_y$  thin films, optical spectroscopy methods, and bandgap determination.

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