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Engineering of the band gap and optical properties of thin films of yttrium hydride

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Thin films of oxygen-containing yttrium hydride show photochromic effect at room temperature. In this work, we have studied structural and optical properties of the films deposited at different deposition pressures, discovering the possibility of engineering the optical band gap by variation of the oxygen content. In sum, the transparency of the films and the wavelength range of photons triggering the photochromic effect can be controlled by variation of the deposition pressure. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4891175>]

Since the discovery of its switchable optical properties in 1996,¹ study of rare-earth metal hydride films have emerged as an interesting research topic, with potential applications in smart windows,^{2,3} hydrogen sensors,⁴ and solar collectors.^{5,6} The driving force for the effect was the switching induced by hydrogen uptake in the films, and the films were capped by a thin layer of Pd in order to speed up this reaction. Later on, photo-induced switching of optical properties has been observed in yttrium hydride (YH_x) films illuminated by visible laser light at pressures of several GPa at room temperature.⁷ Recently, there has been a resurgence of interest in light-induced variation of optical properties of the films when it was observed in YH_x films at atmospheric conditions and without using a thin layer of Pd for capping.⁸ These films will, upon exposing to air, form a thin oxide layer at the surface and substantial amount of O impurities was found to be incorporated into the bulk of the films.^{9,10} The O impurities might play an important role in the optoelectronic properties of YH_x. The O-containing YH_x (hereafter YH:O) films studied in Ref. 8 is unique, since it might show reversible photochromism induced not only by ultraviolet (UV) light, but also from the visible part of the optical spectrum. The issue as to how to control the photon wavelength range triggering the photochromic effect was an important challenge. In our earlier work, we had observed that some films possessed yellowish color whereas others were more transparent—finding way(s) of controlling the transparency of the films was another important challenge. Time-resolved X-ray diffraction (XRD) studies showed a photo-induced structural rearrangement leading to a lattice contraction,¹¹ indicating that the mechanism underlying the photochromic reaction might be not purely electronic.

In this article, we report on the optical and structural properties of YH:O films obtained at different deposition pressures. We show that by controlling the deposition pressure, the optical band gap of the films can be altered, which might be related to the changes in the oxygen content of the samples. Moreover, we discuss how the wavelength range of photons triggering the photochromic effect and the transparency of the films are affected by variation of the oxygen

content. The possibility to tune the optical properties by simply changing the deposition pressure is interesting for technological applications.

The reactive sputtering of the YH:O films was carried out using on-axis pulsed DC magnetron sputtering in a Leybold Optics A550V7 in-line sputtering machine. The DC power applied to the Y target was 1000 W with a pulsed frequency of 70 kHz, in order to prevent arcing and charge accumulation on the target surface during reactive sputtering. The sputter chamber was evacuated down to a base pressure of typically $\sim 10^{-4}$ Pa prior to film deposition. A commercially available Y target (dimensions of 125 × 600 × 6 mm) with a purity of 99.99%, and argon and hydrogen gases with purity 5N and 6N, respectively, were used. The films were deposited at room temperature in a mixed atmosphere of argon and hydrogen at total pressures of 0.4, 1.2, 2.0, 3.0, and 6.0 Pa. No oxygen was intentionally introduced in the chamber during processing. The total gas flow of argon and hydrogen was kept constant at 200 sccm with an Ar:H₂ gas ratio of 4:1. The YH:O films were deposited on glass substrates (Menzel-Gläser microscope slides with a thickness of 1 mm in dimensions of 26 mm × 76 mm). The substrates were cleaned with DI water in an ultrasonic bath and blow-dried with nitrogen before introduced into the load lock chamber. The substrates were transferred into the chamber when the pressure in the load lock was typically below $\sim 10^{-5}$ Pa.

The film thickness was determined using a stylus surface profilometer. The optical properties of the thin films were characterized using an Ocean Optics QE65000 optical spectrometer. In order to induce the photochromic effect, the thin films were illuminated for 1 h by artificial sunlight from a solar simulator with an intensity of 100 mW/cm² at ambient conditions. Grazing-incidence X-ray diffraction (GI-XRD) measurements were carried out in a Bruker D8 Discover X-ray diffractometer, in order to identify the structure and crystal orientation of the films.

Figures 1(a) and 1(b) show the optical transmittance and absorbance for the films deposited at different pressures and before they have been subjected to illumination. The general trend is that the transmittance of the samples increases with increasing deposition pressure. One can see oscillations in the transmittance spectra, which are due to film thickness interference effects. The oscillations

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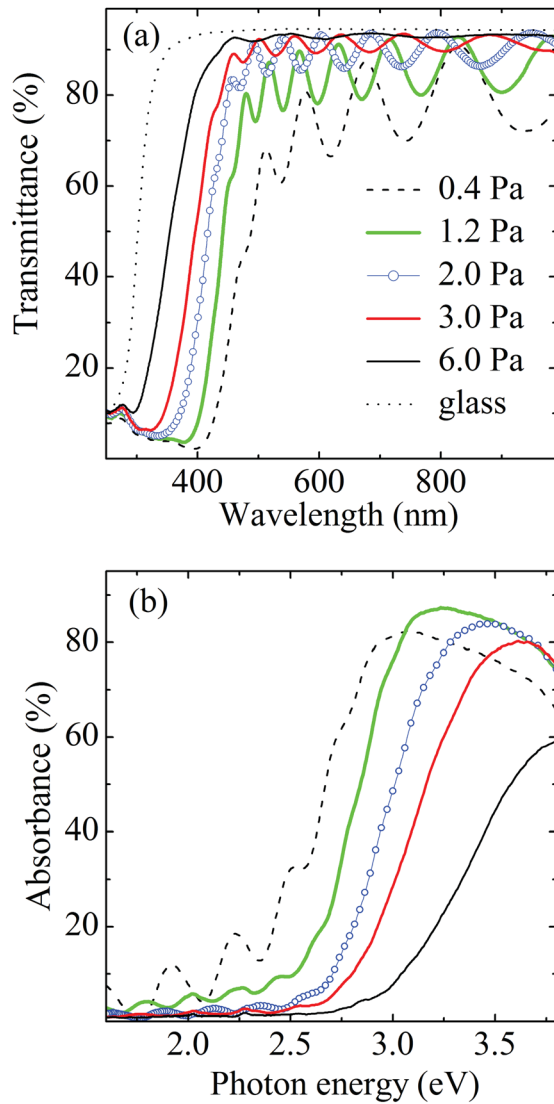


FIG. 1. (a) Optical transmittance as a function of wavelength and (b) absorbance as a function of photon energy for the O-containing YH_x thin films obtained at deposition pressures ranging from 0.4 to 6.0 Pa. The glass substrate is included here for comparison. In the calculations of the absorbance data contribution from the glass substrate is subtracted.

corresponding to the films deposited at different pressures are shifted in phase, which is mainly due to difference in thickness of the films [Table I].

TABLE I. Deposition pressures (in Pa), film thickness (in nm), and direct band gap (E_g^{dir}) (in eV) estimated from transmission spectra for the O-containing YH_x films in transparent state deposited at pressures in the range of 0.4–6.0 Pa.

Sample	Deposition pressure (Pa)	Film thickness (nm)	E_g^{dir} (eV)
YH_3			2.6 ^a
YH:O	0.4	600	2.8
	1.2	1290	2.9
	2.0	1220	3.1
	3.0	1300	3.3
	6.0	870	3.7
Y_2O_3			5.5 ^b
Glass			4.2

^aReference 13.

^bReference 14.

Analysis shows that the transmittance corresponding to the band edge shifts toward shorter wavelengths with increasing deposition pressure. This indicates a change in the optical band gap of the thin films. Table I displays the direct band gaps, E_g^{dir} , estimated from the transmittance and reflectance spectra according to the procedure described in Ref. 12. Analysis shows that E_g^{dir} increases with increasing deposition pressure. The band gap increase is within a wide range of 2.8–3.7 eV for E_g^{dir} , also clearly visible on the color of the films. The estimated band gaps of the films exceed that for oxygen-free YH_3 , which is 2.6 eV.¹³ It increases with increasing deposition pressure up toward the optical band gap of Y_2O_3 , which is 5.5 eV.¹⁴

The large band gap increase can be explained by the level of oxygen incorporated into the films. As we have demonstrated earlier,^{8,9} films prepared by reactive sputtering deposition and not capped by a Pd protection layer contained a substantial amount of oxygen, even though the oxygen incorporation in the film was not done intentionally. Earlier Rutherford backscattering spectrometry and neutron reflectometry measurements indicated a surface oxide layer of 5–10 nm thickness and an oxygen content in the bulk of the film in the range of 8–32 at.% in YH:O samples. It is believed that yttrium reacts with oxygen originating from water vapor that is present in the process chamber during deposition. For example, the water content of the residual gas in a high vacuum system at a base pressure of 5×10^{-5} Pa (our base pressure was $\sim 10^{-4}$ Pa) has been reported to be 97% in the literature.^{15,16} Hence, for the high-pressure deposited samples, it is likely that the oxygen content is even higher when the partial pressure of water vapor is increased. The presence of high oxygen concentration in the films might be the cause for the observed band gap increase. A relationship between the optical band gap and the oxygen content has been reported¹⁷ before for O-containing GdH_3 . It was shown that when the oxygen content was increased from 0 to 19.2, 47.1, and 60 at.% for GdH_3 , $\text{GdO}_{0.6}\text{H}_{1.53}$, $\text{GdO}_{1.3}\text{H}_{0.46}$, and Gd_2O_3 , respectively, the optical band gaps changed from 2.4 to 3.2, 4.8, and 5.4 eV, in excellent agreement with our observations.

We note that upon changing the deposition pressure from 1 to 3 and 6 Pa, no additional reflection peaks were detected by GI-XRD measurements on YH:O films, indicating that all films consist of basically the same type of crystalline material. The main recorded reflection peaks (111), (200), (220), (311), and (331) were indexed with the space group $Fm\bar{3}m$ similar to that known for YH_2 .¹² The intensity of the (200) and the (311) peaks was seen to decrease when increasing the deposition pressure from 1 to 3 Pa. This result might be related to a difference in film texture (orientation) or to a change in the oxygen lattice. Analysis of the XRD data implies a minor change in the structural properties, suggesting that the observed changes in the optical band gap is mainly due to the differences in the oxygen content of the samples.

These findings mentioned above demonstrate the possibility for optical band gap engineering in the thin films of YH:O, which can be controlled by deposition pressure and oxidation. The finding can be useful for controlling transparency of the films from yellowish color corresponding to

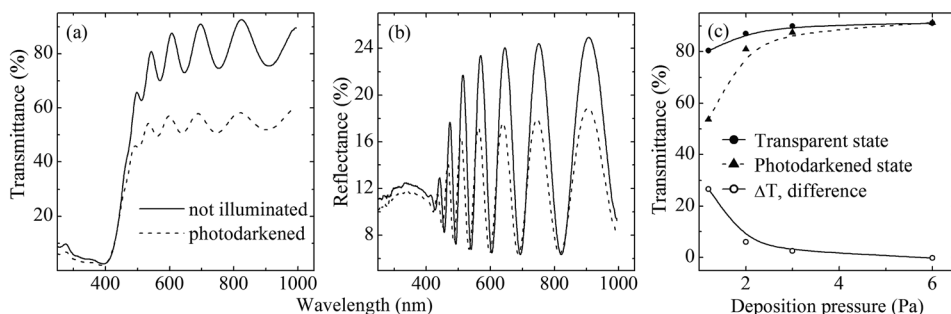


FIG. 2. (a) Transmittance and (b) reflectance spectra for the films deposited at 1.2 Pa before illumination (—) and after the photochromic darkening (---). (c) Average transmittance corresponding to the YH:O films not subjected to illumination (—), after the photochromic darkening (---), and their difference as a function of the deposition pressure.

smaller band gap films close to that of YH₃, to much more transparent films. This is an interesting solution to the challenge related to controlling the transparency in a purposeful way, which might present interest for optoelectronic applications of the films.

Figure 1(b) shows absorbance spectra for the films without being exposed to illumination. One can see a strong absorption peak corresponding to the optical band gap. The intensity of the peak is further increased when decreasing the deposition pressure from 6.0 to 1.2 Pa, and then slightly decreased at 0.4 Pa. Location and long-wave-length edge of the peaks shift toward large photon energies with increasing the deposition pressure, which might be ascribed to increasing the band gap of the films.

Illumination modulates the optical properties of the YH:O films. More specifically, the films will be switched into a photodarkened state. It is therefore interesting to investigate the photochromic effect with respect to the observed changes in the optical band gap and optical properties of YH:O films. Figures 2(a) and 2(b) display representative transmittance and reflectance spectra, respectively, for the films deposited at 1.2 Pa before and after prolonged illumination by the solar simulator. As can be seen, the un-exposed transmittance and reflectance spectra at long wavelengths are larger than those measured after 1 h illumination.

This result is in agreement with the previous findings of Ref. 8. Similar result has been obtained for all films deposited at different pressures. Furthermore, the transmittance spectra of both transparent and photodarkened films oscillated at longer wavelengths of incident photons. However, the oscillations are shifted in phase, which might indicate a photo-induced modulation of the film thickness. More systematic study of this point is needed. This result is consistent with our previous findings¹¹ related to photo-induced lattice contraction of the films.

Figure 2(c) shows the average transmittance in the transparent and photodarkened states as well as their difference in

transmittance ΔT . Here, averaging has been performed for the wavelength range of 500–900 nm. The difference ΔT is a measure of strength of the photochromic response. Analysis shows that the average transmittance in both transparent and photodarkened states was increased with increasing deposition pressure, whereas ΔT decreased and reached zero in the films deposited at 6.0 Pa. This indicates that the photochromic effect is strongly reduced in films deposited at high pressures. The weak photochromic effect might be related to the large band gap of the films, which causes a dramatic reduction in the amount of photons absorbed in the film.

To gain a more detailed insight in difference of optical spectra in transparent and photodarkened states we have subtracted transmittance, absorbance, and reflectance spectra of photodarkened films from those corresponding to transparent films. Figures 3(a)–3(c) show the difference for (a) transmittance ΔT , (b) absorbance $\Delta\alpha$, and (c) reflectance ΔR spectra. Analysis shows that upon illumination of the films, transmission and absorption spectra change drastically whereas the largest change of reflectance due to the photochromic effect is less than 10%. The films deposited at the lowest deposition pressure of 1.2 Pa after darkening strongly absorbed photons with energy smaller than the band gap of YH₃. Such absorption is not available in other films deposited at higher pressures. Also, light absorption of the films in transparent state at photon wavelengths corresponding to band edge seems more enhanced than that in photodarkened state. This result indicates that the absorption of light at photon wavelengths around optical band edge plays an important role in the photochromic effect. In the films deposited at low deposition pressures ≤ 2 Pa, the photochromic effect might be triggered because of the absorption of visible light as well.

In summary, we have studied structural and optical properties of O-containing YH_x films deposited at different pressures in a high vacuum chamber. We found that the increase of the deposition pressure has led to a shift of the band edge towards shorter wavelengths, corresponding to a

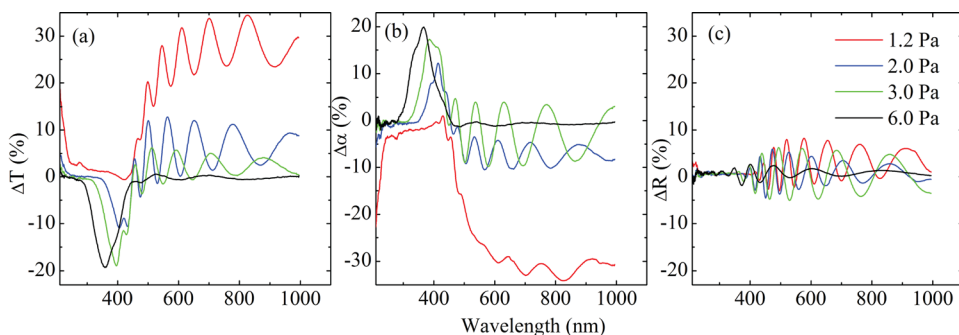


FIG. 3. Difference of the (a) transmittance, (b) absorbance, and (c) reflectance spectra of the transparent film from that after photochromic darkening for the samples deposited at different pressures.

band gap widening in the films. The band gap estimated from optical spectra is found to increase with increasing deposition pressure and is accompanied with a decrease in the photochromic darkening reaction. We conclude that the transparency increases and the band gap shift can be ascribed to the oxygen content. The wavelength range of photons triggering the photochromic effect can also be controlled by the deposition pressures: Mainly by UV light in the films deposited at high pressures and by both UV and visible light in the films deposited at lower pressures. Consequently, the band gap of the material, the transmittance, and the photochromic effect can be engineered by controlling the deposition pressure and the oxygen content.

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