

Photoluminescence properties of photochromic yttrium hydride films containing oxygen

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Abstract

Oxidation of $\text{YH}_{x\pm\delta}$ modulates its optical properties by converting it from optically opaque to transparent state to the visible light and electrical properties from metallic conductivity to insulating. The qualitative change of the materials properties are related to oxidation-induced modulation of electronic properties of the material that will influence on band gap and luminescence properties of the oxygen-containing yttrium hydride (YHO). This work presents the optical properties, studied by optical spectrophotometry and photoluminescence spectroscopy, of YHO thin films deposited by reactive magnetron sputtering at different H_2/Ar flow ratios between 0.18 and 0.28. The indirect and direct band gap of the YHO photochromic films in their clear state has been estimated from optical absorption measurements performed at room temperature, and found in the range between 2.5 and 2.6 eV (indirect allowed transition) and between 3.0 and 3.3 eV (direct allowed transition). The study of photoluminescence (PL) properties has been performed in the temperature range between 10 and 300 K. The luminescence yield corresponding to the clear state was found extremely low in all the YHO films, and it reduced even further once the films darkened under UV-light exposure. The PL emission at room temperature covers the entire UV and visible range, comprising two broad

bands centered at around 2.2 eV and 3.1 eV. The latter band became fine-structured at low-temperatures (10K), showing a series of distinct PL peaks at energy positions between 2.8 - 3.4 eV which were independent on the H₂/Ar flow ratio used during deposition. By the comparison of the PL measurements conducted in vacuum with the ones performed in air, it is possible to conclude that the environment plays an important role in the photochromic properties of YHO. The possible intrinsic and extrinsic origin of the structured PL emission is discussed in terms of excitonic features and/or luminescent surface defects. We report that the main optical transitions of the films deposited at different H pressures did not change by variation of temperature or by UV light-induced color change.

Keywords: Oxygen-containing yttrium hydride films, photoluminescence, photochromism.

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1. Introduction

Rare-earth metal hydride films exhibit many exciting properties that present interest for applications in smart windows [1-2], hydrogen sensors [3], superconductivity [4], and solar collectors [5-6]. Recently, 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]. Such effect was observed by Mongstad et al. [8] in oxidized YH_x ; since then, YHO has attracted more and more research interest [9-14] due to its high transparency in the clear state and its ability to photodarken evenly across the visible spectrum. YHO has promising applications in many fields such as ophthalmology, building and transportation industry, etc. This is relatively new material with mixed anions of O and H bond to cations of Y. The films have been obtained by oxidizing the $\text{YH}_{2\pm\delta}$. In $\text{YH}_{2\pm\delta}$ the Y atoms are in the charge state $2+$. Oxidation has been performed by exposing the $\text{YH}_{2\pm\delta}$ film right after the deposition by magnetron sputtering. So, the incorporation of O atoms into the film is not controlled and can be continued until the Y atoms reaches the charge state $3+$, which is the energetically most favorable one. Since it is hard to reach the $3+$ charge state for all the Y atoms in the film, one can expect many types of structural defects caused by H and O stoichiometry that can be tuned by, e.g., annealing. Furthermore, H and O concentrations in the films are somehow connected to each other. Compositional analysis showed [10] that the concentration of the O and H atoms in the films are anti-correlated. Since both H_2O and O_2 molecules are in the air, the H-terminated $\text{YH}_{2\pm\delta}$ can react with both. So, during the oxidation processes, O and/or O-H can diffuse inside the films that can be detected by the study of vibrational properties.

To date, many interesting properties and phenomena have been reported in YHO resulted in by oxidation of the films: photochromic effect [8], optical bandgap engineering [9], the

enhancement of oxygen concentration in the films with the increase of the hydrogen deposition pressure [10], etc. Mechanism of the photochromic effect in YHO has been suggested to be caused by formation, after intense illumination with blue/UV light, of small metallic domains within the wide band gap-semiconducting YHO lattice [15]. On the other hand, nuclear magnetic resonance studies performed in YHO shown that local hydrogen rearrangements are involved in the photochromic effect [11]; in the photodarkened state, around 3% of the mobile hydrogen ions *freeze out*, reappearing during bleaching. Studies by Doppler broadening positron annihilation spectroscopy (PAS) [12] pointed out to the generation of cation vacancies or vacancy clusters involving generated anion vacancies. However, these vacancies did not relax during the bleaching of the films, showing that the structural changes are not directly responsible for the photochromic mechanism.

Before oxidizing, the $\text{YH}_{x\pm\delta}$ possess dark color and metallic-type electrical conductivity. Upon oxidation, it will become wide-bandgap material ($E_g \geq 2.6$ eV at 300 K [8]), which is transparent to visible light and it exhibits large electrical resistivity above $1 \text{ M}\Omega \times \text{cm}$ [8-9] thus becoming insulator. The huge change in materials properties is caused by alterations in electronic structure and optical properties of the films that can further be tuned by controlling O and H stoichiometry. Photoluminescence studies can be helpful to clarify the role of the H and O structural defects in optoelectronic properties of YOH. However, there are neither reports on luminescence properties, nor any systematic study of the YHO band gap. It should be noted in this respect that the band gap of a material can be estimated from photoluminescence (PL) measurements if the origin of the observed peaks can be attributed to near-band-edge emission (e.g., exciton peak plus its binding energy equals to bandgap). However, for indirect bandgap materials containing luminescent mid-gap and/or surface defects, the near-band-edge features in

PL spectra may be over-dominated by defect-related emission, thus making the band gap assessment inaccurate or impossible. By contrast the absorption spectra, derived from the optical transmittance and reflectance of the material, unambiguously reveals the band-edge, which on its turn provides information on the band gap energy, once the exciton or impurity related absorptions (Urbach tail) are taken into account. Also, it is important to note that the energy of the band gap derived from the optical absorption edge is, in general, higher than the one inferred from PL measurements. This is due to underlying physical processes of absorption and emission in the material (Stokes shift). In the present work, we address the optical absorption and emission properties of YHO thin films deposited by magnetron sputtering at different H₂/Ar flow ratios by using UV-vis spectrophotometry and PL spectroscopy in the temperature range 10-300K.

2. Methods

2.1 Deposition and thickness measurements

As described in our previous work [15], oxygen-containing yttrium hydride films, YHO, have been obtained from the post-deposition oxidation in air of YH_{x±δ} thin films which, on they turn, were deposited by pulsed reactive magnetron sputtering in a Leybold Optics A550V7 sputter unit. The target was a metallic Y plate (99.9% purity) of dimensions 125×600×6 mm. The applied deposition power was 1000 W and the deposition pressure was set to 10⁻² mbar by adjusting the exhaust throttle valve of the chamber. The samples studied in the present work were deposited onto 1mm thick soda lime glass substrates at a H₂/Ar flow ratio of 0.18, 0.21 0.26 and 0.28. Then, the films have been exposed to air where they oxidize. The deposition time was fixed at 30 min, and therefore, the thickness of the films decrease as the sputtering rate decreases with the increase of the concentration of the reactive gas. The final thickness of the films,

determined by an Alpha-Step Stylus profilometer, is 690, 590, 400 and 350 nm for the films deposited at H₂/Ar flow ratios of 0.18, 0.21 0.26 and 0.28, respectively.

2.2 Optical measurements

PL measurements have been performed in the temperature range 10-300 K by using a 325 nm wavelength cw-HeCd laser as an excitation source. The PL emission was collected by a microscope and directed into an imaging spectrometer (Horiba Jobin Yvon, iHR320) coupled with an electron-multiplying CCD camera (Andor, Luca DL-658M EMCCD), with a 0.2 nm spectral resolution, as a detector. The optical absorption coefficient, α , for each sample has been determined from the reflectance, R , and transmittance, T , curves (corresponding to the clear state) [16]. T and R have been measured by using two Ocean Optics spectrophotometers (QE65000 and NIRQUEST512) equipped with an integrating sphere and an Ocean Optics DH-2000 light source at normal incidence. The intensity of this source is not enough to produce a significant darkening of the films.

3. Results

3.1 Direct and indirect band gap

YHO films contain two types of competing anions, oxygen and hydrogen, both connected to yttrium atoms [17]. By performing the deposition at different H₂/Ar flow rates and then oxidizing the films, it is possible to obtain YHO thin films with different concentrations of anion vacancies as well as of hydrogen and oxygen anions with [H] and [O] concentrations anti-correlated [10] with each other. As it was shown in Ref. [9] by the study of transmission spectra, the band gap of the YOH films can be controlled by H₂/Ar flow rates. For quantitative study of

this effect, the estimation of the band gap E_g has been done from the measurements of spectral distribution of the absorption coefficient (α) obtained from the spectrophotometric determination of R and T at room temperature (not shown). Figure 1 displays the Tauc plots for the different samples for the determination of E_g . In particular, indirect allowed and direct allowed energy gaps were calculated by plotting the dependence of $(\alpha h\nu)^{1/2}$ [Fig. 1(a)] or $(\alpha h\nu)^2$ [Fig. 1(b)] as a function of the incident photon energy ($h\nu$), and then by the linear extrapolation to zero of the absorption edge, (depicted in the figure by dashed lines). As expected, the incorporation of oxygen into the metallic YH_2 lattice causes a dramatic opening of E_g [9]. According to Fig. 1 (a), indirect allowed transitions occur at energies ranging between 2.5 and 2.6 eV. On the other hand, the values obtained for the case of a direct allowed transition range between 3.0 and 3.3 eV [Fig. 1 (b)]. The values obtained for the indirect transition are in agreement with the values recently reported by Nafezarefi et al. [13]. The values of E_g obtained by considering a direct transition are comparable to the ones reported for $GdO_{0.6}H_{1.53}$ [18] and for other rare-earth metal-oxyhydrides [13]. Both direct allowed and indirect allowed E_g values have been plotted in the figure insets as a function of the H_2/Ar flow ratio during the deposition process.

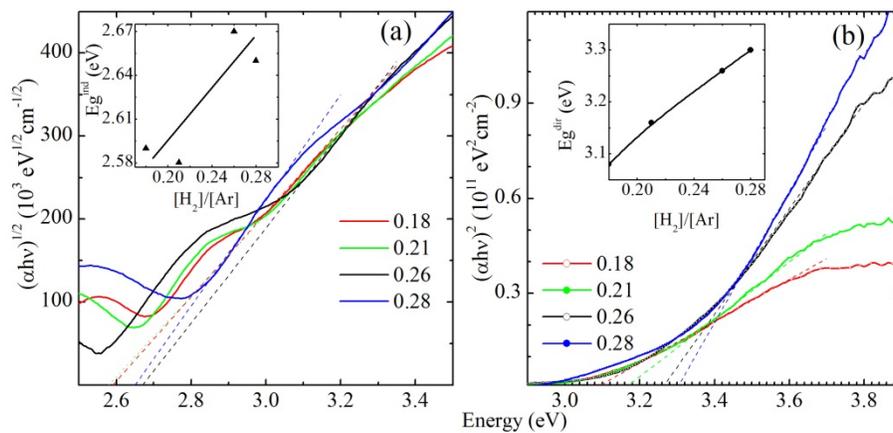


Figure 1. *Tauc plots $(\alpha h\nu)^2$ (a) and $(\alpha h\nu)^{1/2}$ (b) as a function of the photon energy $h\nu$ for YHO films in the clear state. The dashed lines correspond to the linear fits of the band edge absorption curve. Insets in the figure show the variation of E_g as a function of the H_2/Ar ratio.*

3.2 Photoluminescence studies

Figure 2 summarizes PL results obtained at 10 K and 300 K for the YHO films deposited at H_2/Ar flow ratios of 0.18, 0.21, 0.26 and 0.28. For each film, a doublet of PL spectra is shown representing the initial and final (saturated) state reached after prolonged exposure to the 325 nm wavelength of UV probing laser beam. In all the samples, the luminescence yield is extremely low in the initial stage, and it is further reduced over time during the measurement, as a result of the films' photodarkening, caused by the laser probing beam. The room-temperature PL emission covers the entire UV-visible range, comprising two broad bands centered at around 2.2 eV and 3.1 eV, as can be observed in Fig. 2(a). The UV component, on the other hand, becomes fine-structured at low-temperatures, showing a series of distinct peaks in the range 2.8 - 3.4 eV at energy positions apparently independent on hydrogen-to-argon flow ratios [Fig. 2(b)]. The PL spectra taken at 10 K contain at least seven peaks, all seemingly separated by ~ 85 meV, being the four most prominent peaks located at $E_1=3.34$ eV, $E_2=3.18$ eV, $E_3=3.0$ eV, and $E_4=2.8$ eV. Such peak periodicity might be an indication of phonon-assisted optical transitions, i.e., multiple phonon replicas of a possible exciton line located at $E_x=3.34$ eV. On this basis, the n -order replicas would be located at energies $E_x - 2n\hbar\nu$, where $\hbar\nu$ is phonon energy equal to ~ 85 meV. Of course, the exciton origin of the peaks remains speculative unless proved experimentally. The alternative model of structured UV-emission would involve solely surface-related luminescent

defects, possibly both of intrinsic nature (vacancies, dangling bonds, etc.) and extrinsic (adsorbed species on the surface).

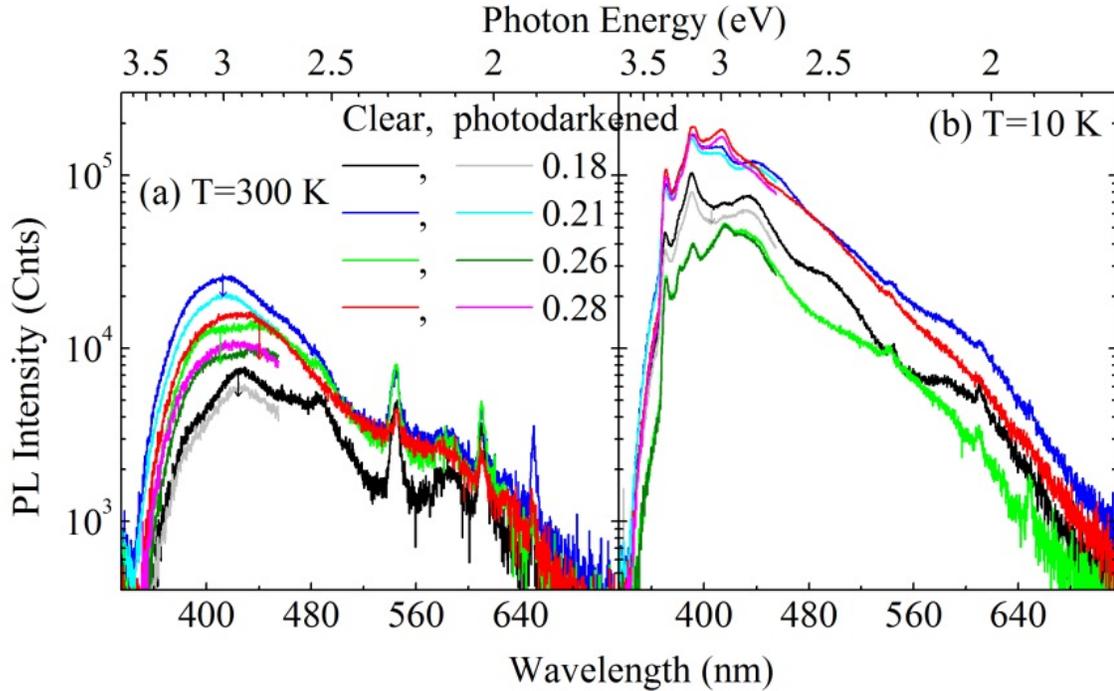


Figure 2. PL spectra taken at (a) 300 K and (b) 10 K for the YHO films deposited at H₂/Ar flow ratios of 0.18, 0.21, 0.26 and 0.28 before and after UV light-induced darkening.

As already mentioned, the photochromic effect in YHO is associated with the formation of metallic phase domains within the semiconducting lattice; thus, the photodarkening of the films is expected to affect the PL efficiency. Indeed, the integrated PL intensities of the photodarkened films are observed to be around a 35 % lower than those of the initially transparent films. The deposition of yttrium hydride by sputtering at different H₂/Ar flow ratios leads to different concentrations of H vacancies, which will attract equivalent amount of O atoms into the films [9-10] and affect the films' porosity. In turn, the porosity enhances the role of surface defects that may change the density of states around the band edges, influencing both radiative and non-

radiative recombination pathways. In Fig. 2, the strong variation of the E₁-E₄ peak intensities of the YHO films deposited at different H₂/Ar flow ratios can be observed. However, there is no indication of the formation of new defects that may create new peaks in the PL spectra.

Figure 3 summarizes temperature-dependent PL measurements in the range 10-300 K for the YHO film deposited at an H₂/Ar flow ratio of 0.28. The monotonic decrease of the PL intensities with increasing the temperature from 10 K to 300 K is observed in the data. The estimation of the activation energy for thermal quenching of the PL intensity has been obtained by the analysis of the intensities of particular peaks as a function of the temperature. Such estimation has been performed for the dominant peaks, E₁ and E₂, but also for the total integrated PL intensity, as shown by the Arrhenius plot depicted in Fig. 3(b). The numerical fitting of the results points to an activation energy of ~60 meV for all the cases. This suggests that the same non-radiative recombination mechanism can be responsible for the thermal quenching of the E₁, E₂ and the total integrated PL intensity.

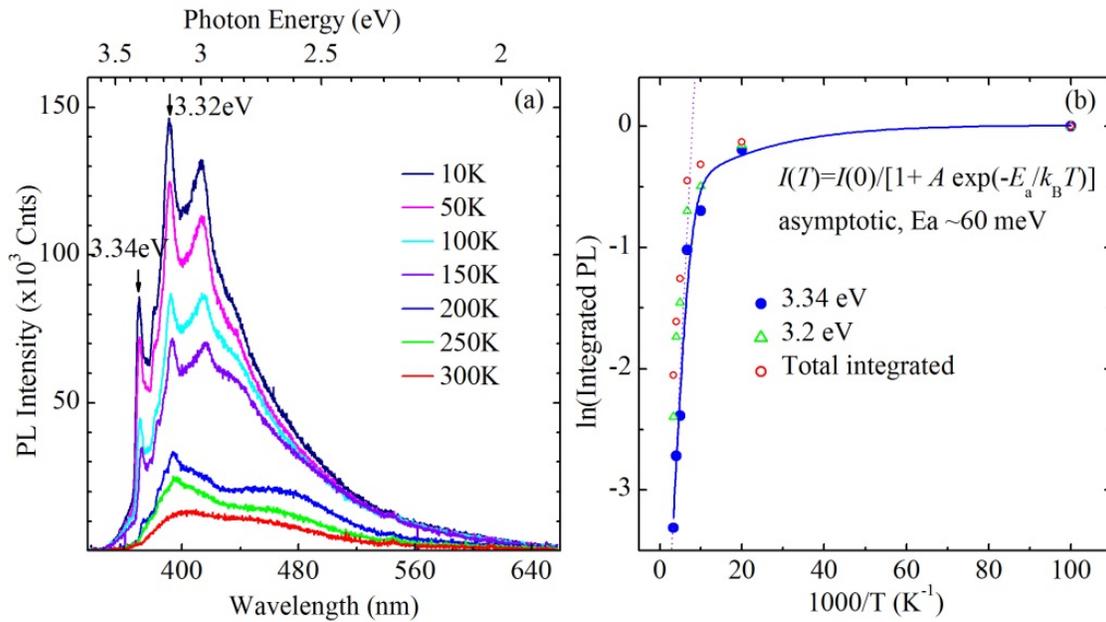


Figure 3. *PL spectra for the YHO films deposited at a H₂/Ar flow ratio of 0.28 (a) measured at different temperatures and (b) the Arrhenius plot of the dominant peaks and integrated PL intensity.*

3.3 Influence of ambient

In order to study the influence of the ambient, Figure 4 compares the PL spectra of the YHO films, deposited at a H₂/Ar flow ratio of 0.28, measured in air and vacuum. The PL spectra measured at 300K in vacuum and in air notably differ from each other; indeed, the integrated PL yield in air is reduced when compared to the one measured in vacuum. This result indicates important role of the surface effects in optical properties of YHO films and/or the presence of a source of oxygen atoms. The photochromic effect possibly relies not only the bulk materials properties, but also involves surface [19]. Indeed, when organic molecules such as, e.g., aldehydes, formaldehydes, alcohols, organic acids, etc., containing O with unshared electron pair in a *p* orbital are adsorbed on the surface of YHO, a coordination bond can be formed between them. Upon illumination by UV light, the unshared electron pair of the oxygen atom of the adsorbed molecule can be pulled into a vacant inner *d* orbital of a superficial Y atom, thus weakening the intramolecular bonds and facilitating the transformations within the adsorbed molecule. The light-induced change of the charge state of the Y atoms can cause rearrangement of the local lattice in their vicinity and lead to the formation of domains that would provide dark color to the film. This particular mechanism of photochromic effect in the YHO will be the topic of future studies.

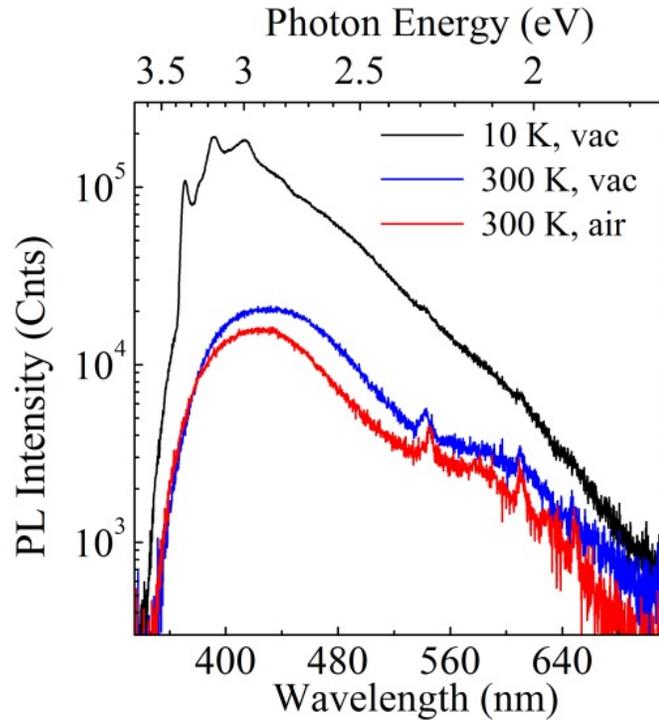


Figure 4. *PL spectra taken in vacuum and in air at 300 K for the oxygen-containing yttrium hydride deposited at H_2/Ar flow ratio of 0.28. Low-temperature PL spectrum obtained in vacuum at 10K is also presented for reference.*

Conclusion

The optical emission and absorption properties of reactive sputter deposited oxygen-containing yttrium hydride (YHO) thin films has been studied by spectrophotometry and photoluminescence (PL) spectroscopy. According to these measurements, YHO presents an indirect allowed band gap between 2.5 and 2.6 eV. On the other hand, higher energy values for the band gap, between 3.2 and 3.3 eV, have been obtained if a direct allowed transition is

considered. In addition, the PL properties of the YHO films deposited at different hydrogen flow rates have been studied in the temperature range 10-300 K. The luminescence yield of the films in the transparent state is found extremely low. This intensity is even lower in the photodarkened films. The room-temperature PL emission spectra observed covers the entire UV-visible range comprising two broad bands centered at around 2.2 eV and 3.1 eV. The UV component becomes fine-structured at low-temperatures showing a series of distinct PL peaks between 2.8 - 3.4 eV and at energy positions independent on the hydrogen-to-argon ratio used during deposition. By comparing the PL measurements conducted in vacuum and in air, we conclude that surface states and/or the presence of a source of oxygen play an important role in optical properties of YHO films. We discuss possible intrinsic and extrinsic origin of the structured PL emission in terms of excitonic features involving higher-lying direct band and/or luminescent surface defects. Our analysis showed that the main optical transitions of the films deposited at different H pressures did not change by variation of temperature or by UV light-induced color change.

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