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Photochromic YO_xH_y Thin Films Examined by *in situ* Positron Annihilation Spectroscopy

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Doppler broadening positron annihilation spectroscopy depth profiles were collected on photochromic YO_xH_y thin films. *In situ* UV illumination of photochromic semiconductor YO_xH_y films leads to an increase in S -parameter and a large reduction in W -parameter, possibly caused by a change in the charge state of vacancies or the growth of hydrogen-rich metallic $Y(O_x)H_y$ clusters, albeit that vacancy formation or changes in positronium formation during illumination might also play a role. Intriguingly, both the S - and W -parameters increase during thermal bleaching, indicating that another process takes place. The Doppler parameters do not return to their initial values after complete thermal bleaching, suggesting that persistent local rearrangements of vacancies and possibly hydride ions have occurred during the full photodarkening–thermal bleaching cycle. Positron annihilation lifetime spectroscopy shows that a small fraction of positronium is formed in as-deposited YO_xH_y films, indicating that the films contain some nanopores.

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1. Introduction

Positron annihilation spectroscopy (PAS) methods based on low-energy positron beams are sensitive probes for thin film energy materials. The depth range accessible to low-energy positron beams, typically up to a few μm below the sample surface, is very suitable to probe current and emerging thin film solar cells and optical hydrogen sensors. PAS detects electronic structure properties associated with the annihilation electrons, and is highly sensitive to the presence of neutral and negatively charged vacancies. Recently, we investigated various types of functional layers for thin film solar cells, including CdSe quantum dot (QD) layers for QD-based solar cells [1], demonstrating that the high sensitivity of positrons to detect surface properties of the QDs stems from the presence of a positron surface state. The degradation of ZnO/Cu(In,Ga)Se₂ [2] and of methyl ammonium lead iodide (MAPbI₃) perovskite solar cells [3] was linked to the in-diffusion of water molecules and to the interplay of the subsequently occurring chemical reactions and vacancies in the ZnO and MAPbI₃ layers. Finally, PAS is very useful for the investigation of hydrogen energy materials, such as Mg_{1-y}Ti_yH₂ thin films [4].

The YO_xH_y materials investigated in this study are derived from the yttrium hydride family. In 2011, Mongstad et al. [5] discovered that semiconducting yttrium oxyhydride films exhibit a unique photochromic effect. The photochromic effect is characterized by a reduction of the optical transmittance upon exposure of YO_xH_y films to UV illumination with photon energies above the band gap. The transmittance is reduced over a broad range of photon wavelengths including the visible and near IR spectral range [5, 6]. Under ambient conditions, photodarkened films reversibly bleach back thermally towards the initial transparent state when the UV excitation is removed, indicating that YO_xH_y and other rare-earth oxyhydrides are promising for application in smart windows [6]. A recent extensive study by Cornelius et al. [7] reports on the detailed structural and compositional evolution of Y/YH_x/YO_xH_{3-2x}/Y₂O₃ films upon varying the oxygen-to-hydrogen ratio in the Y–H–O ternary phase diagram [7]. Our previous study showed that the trends in the positron Doppler S - and W -parameter of Y/YH_x/YO_xH_{3-2x}/Y₂O₃ thin films strongly correlate with the variation in their electronic structure, ranging from metallic and semiconducting nature to a wide-bandgap insulator with increased O:H ratio [8]. Here, we report PAS measurements during an *in situ* UV illumination experiment on a photochromic YO_xH_y thin film.

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2. Experimental

YO_xH_y thin films on fused silica (f-SiO₂) substrates were prepared by reactive DC magnetron sputtering of metallic Y targets at 200 W in an Ar/H₂ mixture with 12.5 vol.% of H₂ in an AJA International ATC 2400 magnetron sputtering system at Ar deposition pressures of 0.5 Pa [5, 6, 9]. The oxyhydride phase of the YO_xH_y films results from post-oxidation of the $\text{YH}_{2-\delta}$ films in ambient air. The results reported here were obtained on two YO_xH_y films with a thickness of 330 nm and of 385 nm, and an optical band gap of ≈ 2.6 eV.

The Doppler broadening positron annihilation spectroscopy (DB-PAS) [10] measurements were performed using the variable energy positron (VEP) facility of the Reactor Institute Delft. Depth-profiles were collected using positron implantation energies in the range of 0.1–25 keV. A liquid-nitrogen-cooled high-purity Ge (HPGe) detector with an energy resolution of 1.3 keV was used to determine the energy of the emitted annihilation γ -rays. The momentum windows used to deduce the S parameter and W parameter are $p_L < 0.41$ a.u. (1 a.u. = $7.2974 \times 10^{-3} m_0 c$) and 1.12 a.u. $< p_L < 3.21$ a.u., respectively, with longitudinal momentum $p_L = 2\Delta E/c$ and ΔE the Doppler shift in energy of the detected annihilation γ -ray. The S parameter is a measure of positron annihilation with valence electrons, which provides sensitivity to the electronic structure and the presence of open volume defects such as vacancies or vacancy clusters. The W parameter is a measure of annihilation with (semi-)core electrons which provides chemical sensitivity to the positron trapping site. For *in situ* experiments, a 385 nm LED (M385LP1, Thorlabs GmbH) was fitted with a Köhler lens system and mounted to a UV transparent viewport ($T_{385 \text{ nm}} \approx 90\%$) at the VEP setup for illumination of the YO_xH_y samples through the UV transparent fused silica substrate ($T_{385 \text{ nm}} = 92\%$). The typical UV irradiance at the sample position was 31 mW/cm² as measured with a calibrated USB-2000+ spectrometer (Ocean Optics B.V.). The same UV excitation parameters were used during separate transmittance measurements in order to characterize the photochromic contrast and thermal bleaching speed of the samples prior to DB-PAS investigations. The optical transmittance measurements were performed using an Ocean Optics DH-2000-BAL deuterium-halogen UV-vis-NIR light source (230–2500 nm) and an Ocean Optics HR4000 energy-dispersive detector (190–1100 nm).

Additional *ex situ* positron annihilation lifetime spectroscopy (PALS) [10] experiments on similar as-deposited samples were performed without UV illumination at selected positron energies between 1 to 18 keV using the pulsed low-energy positron lifetime spectrometer (PLEPS) instrument of the neutron induced positron source (NEPOMUC) facility at the Heinz Maier-Leibnitz Zentrum (MLZ) research reactor in Garching.

3. Results and discussion

In Fig. 1a we compare the optical transmittance spectra of the YO_xH_y sample with a thickness of 385 nm in the as-deposited state, after photodarkening for 2 h under 31 mW/cm² UV illumination and after subsequent bleaching for 4 h and 17 h. Time-dependent measurements showed that thermal bleaching occurs on a time scale of the order of ≈ 20 h ($\tau_{\text{bleach}} \approx 4$ h). Indeed, transmittance spectra collected on the 330 nm sample studied in the *in situ* PAS measurements demonstrate that the 3 days of bleaching in vacuum during the PAS measurement is sufficient to reach a nearly full recovery of the initial transmittance, indicating reversibility of the optical properties (Fig. 1b).

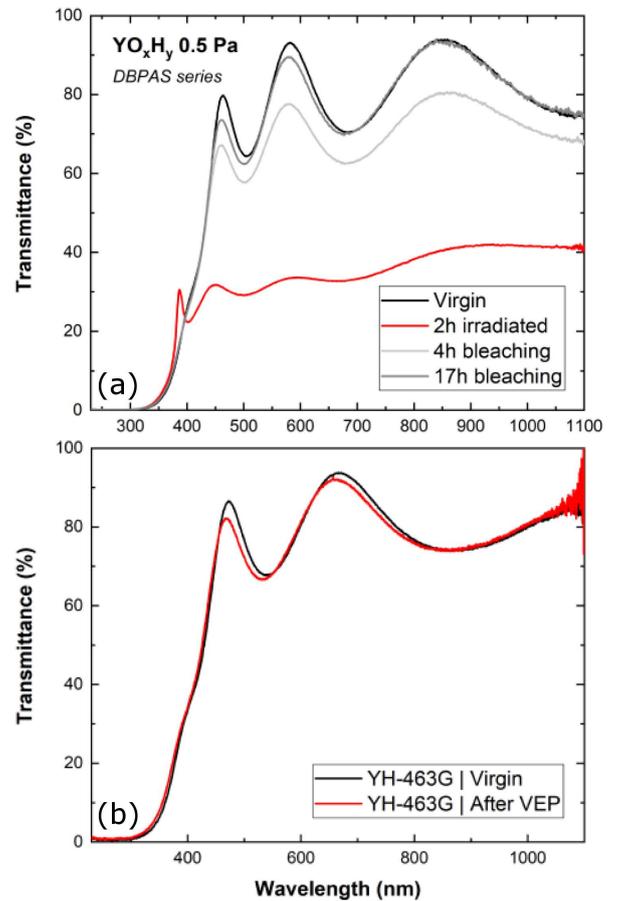


Fig. 1. (a) Optical transmittance spectrum of an YO_xH_y sample with a thickness of 385 nm deposited at 0.5 Pa in (i) the as-deposited virgin state and (ii) the state after 2 h of UV-illumination and (iii) after bleaching for 4 h and 17 h. The peak at 385 nm under UV illumination is caused by stray light of the LED light source. (b) Optical transmittance spectrum of the YO_xH_y sample with a thickness of 330 nm deposited at 0.5 Pa in (i) the as-deposited virgin state (black line) and (ii) the state after 2 h of UV-illumination and 3 days of bleaching in vacuum *in situ* during the PAS experiment (red line).

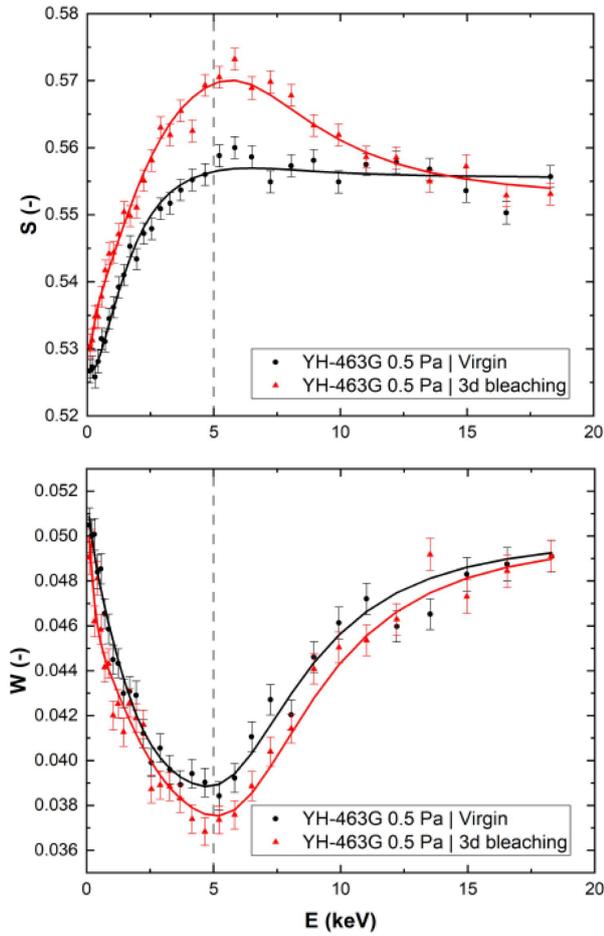


Fig. 2. Positron Doppler broadening S - and W -parameter depth-profile of the 330 nm YO_xH_y sample in (i) the as-deposited virgin state (black circles) and (ii) the state after 2 h of UV-illumination and 3 days of bleaching during the *in situ* PAS measurements (red triangles).

In Fig. 2, the positron Doppler S -parameter depth-profile of the as-deposited 330 nm YO_xH_y sample is compared to the corresponding depth-profiles after 2 h UV-illumination and subsequent bleaching for 3 days during the *in situ* PAS measurements. In contrast to the transmittance spectra, that show nearly full reversible behavior of the photochromic effect on a timescale of ≈ 20 h, the depth profiles show pronounced (semi-)permanent changes after 3 days of bleaching. The S -parameter of the YO_xH_y film, as deduced from VEPFIT analysis, has increased by $\frac{\Delta S}{S}|_{\text{final}} = +3.0 \pm 0.5\%$, whereas the W -parameter shows a modest decrease of $\frac{\Delta W}{W}|_{\text{final}} = -5 \pm 1\%$.

In order to understand the significance of these changes, we examined the state of as-deposited YO_xH_y films prepared in the same manner by PALS measurements using the PLEPS spectrometer at the MLZ Garching research reactor. The PALS spectra on a 0.5 Pa YO_xH_y film with a thickness of ≈ 290 nm indicate the

presence of a fast component with an average lifetime of around 270 ps, that most likely stems from annihilation in defect-free YO_xH_y regions and in yttrium cation mono-vacancies (V_Y). Furthermore, positronium was observed with a lifetime of ≈ 1.7 ns and an intensity at 4 keV of $\approx 4\%$, indicating that the films contain nanopores with a diameter of ≈ 0.5 nm, assuming a spherical shape.

The apparently irreversible changes in S and in W after full optical bleaching therefore most likely stem either from additional formation of V_Y cation vacancies, or, alternatively, of small vacancy clusters involving anions, such as V_Y-V_H . H^- hydride ions in similar types of rare-earth oxyhydrides are (locally) rather mobile [11, 12] and therefore, H^- ions might have irreversibly moved to hydrogen trapping sites in e.g., the nanopores during the illumination. Clearly, *in situ* illumination studies using PALS may aid to reveal which type(s) of open volume defects in the YO_xH_y films are generated in an apparently irreversible way during a full photodarkening–bleaching cycle.

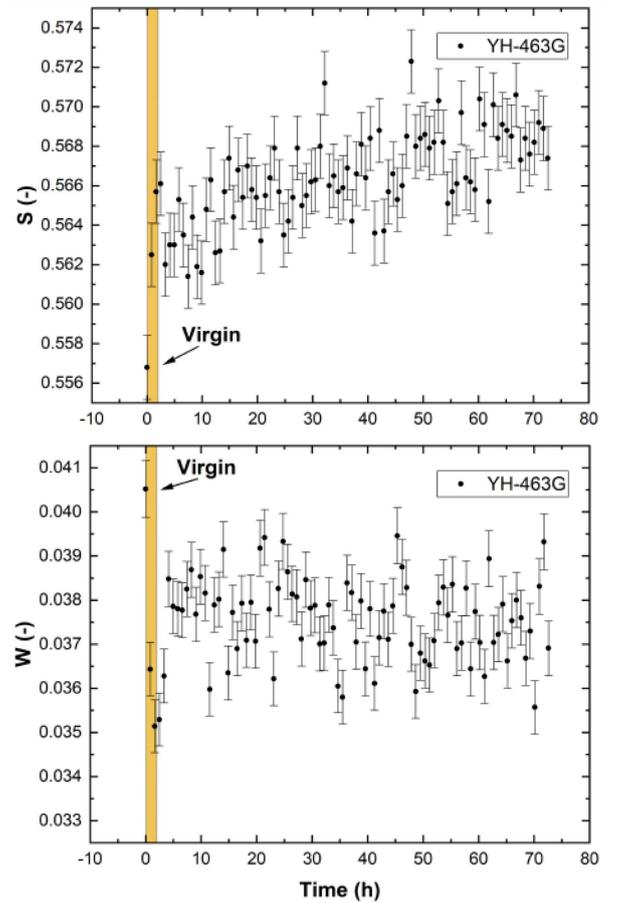


Fig. 3. Time-dependence of the Doppler S - and W -parameter collected at a positron implantation energy of 5 keV. The orange-shaded area denotes the time interval of 2 h of *in situ* UV optical illumination of the 330 nm YO_xH_y sample, after which the LED ($\lambda = 385$ nm) is turned off and the sample bleaches in dark conditions.

Figure 3 presents the time-dependence of the S - and W -parameter collected at a fixed positron implantation energy of 5 keV, corresponding to a mean positron implantation depth in the center of the YO_xH_y film, during 2 h of photodarkening (orange area) and subsequent bleaching for 70 h, in comparison with the S - and W -parameter in the initial state. The Doppler parameters show clear changes during illumination that are quite different from those observed after full optical bleaching. A relatively small change in S -parameter of only $\frac{\Delta S}{S}|_{\text{ill.}} = +1.4 \pm 0.3\%$ is observed after 2 h of illumination, while the W -parameter shows a strong decrease of $\frac{\Delta W}{W}|_{\text{ill.}} = -12 \pm 2\%$, i.e., about twice larger than the observed (semi-)permanent change in W .

The remarkable changes in the Doppler parameters during UV illumination may stem from either of the following possible causes, including (i) charging of positively charged vacancy levels by photo-excitation of valence band electrons $V^{(+)} + e^{-} \rightarrow V^{(o)}$, leading to the presence of positron-trapping neutral vacancies, (ii) the formation of hydrogen-rich metallic $\text{YH}_{2-\delta}$ or $\text{YO}_x\text{H}_{3-2x}$ ($x > 0.5$) clusters [7], perhaps caused by photo-induced local transport of H^{-} and local phase segregation, (iii) changes in the formation of positronium due to the presence of photo-excited charge carriers in the photochromic state. Also, formation of vacancies by the UV illumination cannot be excluded. *In situ* PALS studies and *ab initio* modeling [10] of positron lifetimes and positron-electron momentum distributions may provide the necessary additional information to identify the positron annihilation site. This would enable to discriminate between the indicated possible atomic-scale transformations, providing quantitative insights into the local transformations that accompany the photochromic darkening and that possibly contribute to its mechanism.

4. Conclusions

In situ optical illumination of photochromic YO_xH_y films above the band gap leads to significant changes in the positron Doppler S - and W -parameters, that might point to a change in the charge state of vacancies or to local segregation of metallic nanoclusters due to hydrogen migration, albeit that formation of vacancies can also occur. Intriguingly, during thermal bleaching both the S - and W -parameters are seen to increase, and thus do not return to their initial values after a full photodarkening–thermal bleaching cycle. The overall change in S and W compared to the as-deposited state suggests persistent local rearrangements of vacancies and possibly of hydride ions. PALS shows that a small fraction of positronium

is formed in as-deposited YO_xH_y films, pointing to the presence of nanopores. (*In situ*) PALS studies and *ab initio* calculations may aid to discriminate between the proposed atomic-scale transformations, that could play a fundamental role in the remarkable photochromic properties of the YO_xH_y films.

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