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Excellent photochromic properties of an oxygen-containing yttrium hydride coated with tungsten oxide (YHx:O/WO_3)

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ABSTRACT

Oxygen-containing yttrium hydride films (YHx:O) show interesting photochromic properties under ultraviolet irradiation. In this paper, oxygen-containing yttrium hydride films covered with tungsten oxide were prepared by a direct current magnetron sputtering method. This composite material showed reversible photochromic properties. Furthermore, its coloration speed was faster than that of a single layer of yttrium hydride, and its switching modulation was broader. The photochromic mechanism of the YHx:O/WO_3 thin films was investigated by X-ray diffraction, X-ray photoelectron spectroscopy and energy-dispersive X-ray spectroscopy analysis. Oxygen and hydrogen played a key role in the photochromic process of the YH_x:O/WO_3 composite films.

Yttrium top-covered with palladium thin films showed reversible optical properties after hydrogenation [1]. Ohmura et al. [2] observed that yttrium hydride also has an attractive photochromic behavior. The YH_3 was prepared under a high pressure of ~20 GPa, which is needed for the transformation of YH_3 (hcp) to YH_3 (fcc) [3–5]. The pure YH_3 (hcp) did not show optical change after illumination [2]. Recently, YH_3 (fcc) thin films were obtained under ambient pressure and room temperature by Mongstad et al. [6]. The optical transmittance of the material could be reversibly changed by illuminating it with light. The thin films were prepared by a reactive magnetron sputtering method in a gas mixture of argon and hydrogen. Although the reaction atmosphere did not contain oxygen, the film was oxygen rich, which has played an important role in the photochromic process in previous studies [7,8].

The initial state of the oxygen-containing yttrium hydride films showed a yellowish transparent color in the visible light region. After exposure to light for 1 h, the transmittance of the films diminished in the visible and near-IR region and the electric resistance of the films also decreased, which showed that the initial semiconductor films transformed into metal films. When left in the dark, the films could be recovered to their initial state at a slower speed than the excitation rate [6]. However, the significant optical modulation needed exposure to a solar simulator (air mass (AM) 1.5) with an intensity of 0.1 W/cm^2 for approximately 1 h, which is too slow for industrial applications.

In our study, we prepared a new thin film with excellent photochromic properties. This material consisted of oxygen-containing yttrium hydride thin films covered with WO_3 and showed excellent optical change after short illumination times. Tungsten oxide is a popular photochromic material [9,10]. Several photochromic models have been proposed to explain the photochromic mechanism [11]. The model based on the correlation between optical modulation and double insertion/extraction of ions and electrons has been accepted by most researchers [12]. Through the interaction between the two layers, the sample colored with the optical modulation. At the same time, an interesting change was observed in the YHx:O/WO_3 films before and after illumination; this phenomenon may be helpful to explain the photochromic mechanism of the YHx:O thin films.

The oxygen-containing yttrium hydride was prepared on a glass substrate by a direct current (DC) magnetron sputtering method. Metal targets of Y (99.99%, Φ: 2 in.) and W (99.99%, Φ: 2 in.) were set in the deposition chamber. Firstly, oxygen-containing yttrium hydride thin films were deposited by DC magnetron sputtering of the Y targets in an atmosphere with argon (purity 6 N) and hydrogen (5 N) gas. The base pressure of the deposition chamber was less than 5.0×10^{-5} Pa, and the working pressure during deposition was maintained at 0.4 Pa by controlling the mass flow of Ar/H_2 (10:1). Secondly, a thin film of WO_3 was deposited with W targets on the yttrium hydride under a deposition pressure of 1 Pa by controlling the mass flow of Ar/O_2 (4:1). All the deposition processes were performed without breaking the vacuum.

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The optical transmittance spectra were measured at a wavelength of 350–2600 nm using an optical spectrophotometer (Hitachi High-Technologies U-4100). The illumination process was performed with a xenon lamp (PLS-SXE 300(UV)). The microstructure of the thin films was studied by XRD (Rigaku Ultima IV diffractometer with grazing angle mode using CuKα radiation, λ = 0.15418 nm). X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific Co. Inc., ESCA lab250) was employed to analyze the chemical states and electronic structures. In addition, the distribution of each element in the two layer films was determined by energy-dispersive X-ray spectroscopy (EDS) analysis.

Fig. 1 shows the transmittance of the YHx:O, YHx:O/WO_3, and WO_3 thin film samples before and after UV illumination for different time periods. To assess the visual properties and solar energy-saving properties, the luminous transmittance (T_{lum}, 400–700 nm) and solar transmittance (T_{sol}, 350–2600 nm) were obtained based on the measured spectra, using the following equation:

$$T\rho = \int \psi_\rho(\lambda)T(\lambda)d\lambda / \int \psi_\rho(\lambda)d\lambda,$$

in which $T(\lambda)$ is the transmittance at wavelength λ, ρ denotes lum or sol as appropriate for the calculation, ψ_{lum} is the spectral sensitivity of the light-adapted eye, and ψ_{sol} is the solar irradiance spectrum for AM 1.5, corresponding to the sun standing 37° above the horizon.

The details of the optical properties are listed in Table 1. As shown in Fig. 1(a), the YHx:O film is initially yellowish and transparent. There is no obvious change in its transmittance after illumination for 10 min; there is a significant decrease of the T_{sol} by 28.17% and the T_{lum} by 37.48% after illumination for 60 min. The YHx:O/WO_3 films had a similar surface as that of the transparent YHx:O films. Interestingly, the T_{sol} rapidly decreased by 43.48% and the T_{lum} significantly decreased by 29.92% after exposure to light for only 10 min. No obvious change in transmission was observed after further illumination for 15 min, which indicated that the biggest change in the film's color occurred after illumination for 10 min, as shown in Fig. 1(b).

Table 1
The change in the optical properties of the YHx:O, YHx:O/WO_3, and WO_3 films after illumination.

Sample	YHx:O	YHx:O/WO_3	WO_3
T_{sol} (%) (B-L)	71.95	68.37	81.74
T_{lum} (%) (B-L)	77.21	62.09	77.47
T_{sol} (%) (A-L)	43.78	24.8	76.21
T_{lum} (%) (A-L)	39.73	32.17	74.47
ΔT_{sol} (%)	28.17	43.48	5.53
ΔT_{lum} (%)	37.48	29.92	3

Notes: T_{sol} (%) (B-L) and T_{lum} (B-L) represent the solar and luminous transmittance of the films before illumination; T_{sol} (%) (A-L) and T_{lum} (%) (A-L) represent the solar and luminous transmittance of the films after illumination. The illumination time is 60 min for the YHx:O and WO_3 thin films, and 15 min for the YHx:O/WO_3 respectively. ΔT_ρ represents the biggest transmittance modulation of the different films before and after illumination during the solar and luminous transmittance, obtained by T_ρ (%) (B-L) − T_ρ (%) (A-L).

During the photochromic process, the YHx:O/WO_3 thin films transformed from a yellowish transparent state to a darkened blue state. This color change of the YHx:O/WO_3 thin films after illumination was the same as the photochromic response of the WO_3 films. To ensure that this result was not triggered by the WO_3 single-layer photochromism phenomenon, the optical transmission of the WO_3 thin film was also measured under the same conditions. As shown in Fig. 1(c), there was no obvious change in the transmittance, regardless of the illumination time of the WO_3 film. Therefore, the excellent photochromic modulation of the YHx:O/WO_3 thin films after short illumination time was

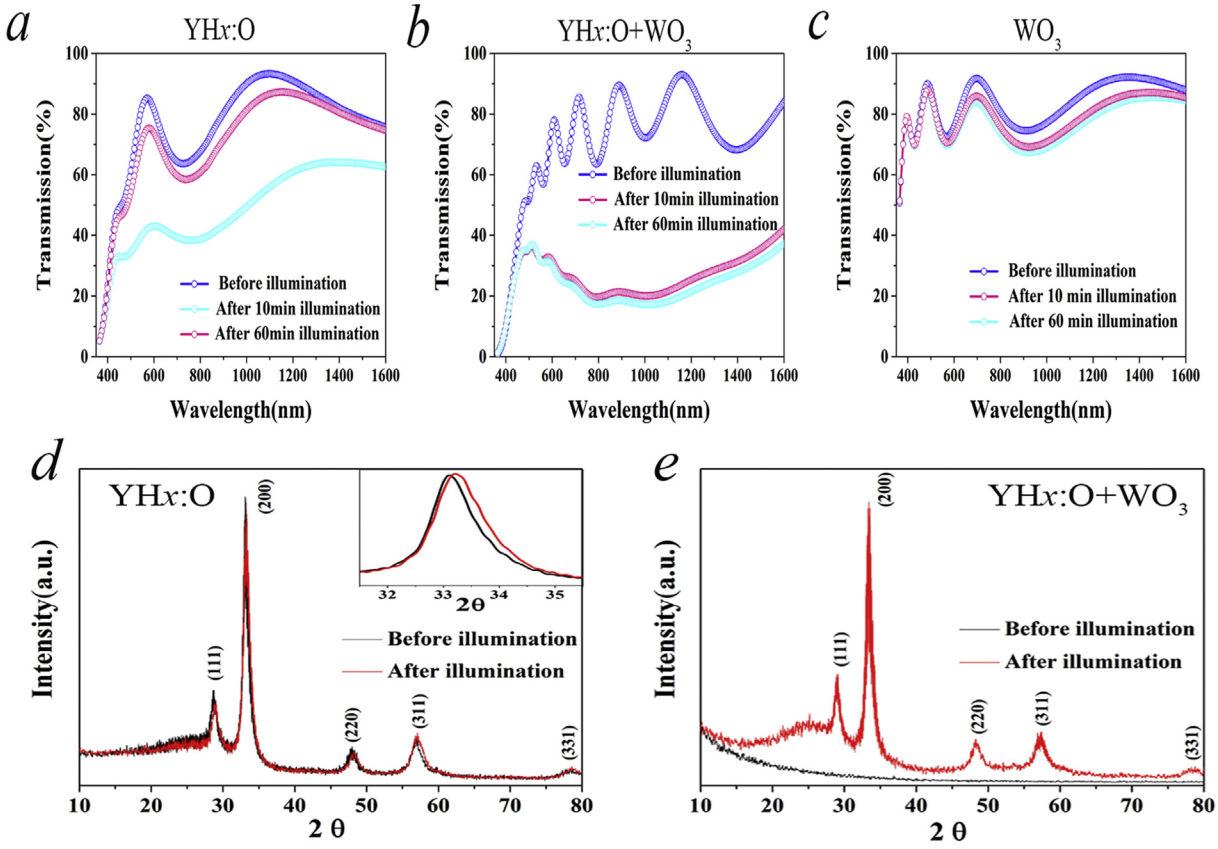

Fig. 1. Optical transmittance spectra (a, b, c) and XRD spectrum (d, e) of the YHx:O films (a, d), YHx:O/WO_3 films (b, e), and WO_3 films (c) before and after illumination by a xenon lamp for different time periods. The thickness of the YHx:O and WO_3 films was 227 and 82 nm, respectively.