ARTICLE IN PRESS

Solar Energy Materials & Solar Cells (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Preparation of yttrium hydride-based photochromic films by reactive magnetron sputtering

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ARTICLE INFO

Keywords:
Yttrium hydride
Photochromism
Smart windows
Thin films
Sputtering

ABSTRACT

Photochromic oxygen-containing yttrium hydride has been synthesized using a two step process. The process consists of an initial sputter deposition of oxygen-free yttrium hydride YH_x, followed by a controlled reaction with air that causes incorporation of oxygen into the material. An *in-situ* study of the YH_x as it reacted with oxygen was made possible by applying an aluminium capping layer with a low but non-zero oxygen permeability prior to air exposure. During the reaction, the visual appearance of the YH_x went from dark and opaque to transparent and yellowish. This transition was accredited incorporation of oxygen into the material, as shown through analysis with energy dispersive x-ray spectroscopy (EDS) and x-ray photoemission spectroscopy (XPS). Grazing incidence x-ray diffraction (GIXRD) studies revealed an *fcc* structure both before and after oxygen exposure, with a lattice parameter that increased from 5.2 to 5.4 Å during the reaction. With the lattice parameter in the oxygen free YH_x being equal to that reported earlier for YH_2, our findings suggest that the non-reacted YH_x in this study is in-fact YH_2.

1. Introduction

Smart windows based on chromogenic materials have in recent years emerged as promising candidates for the next generation of energy-efficient windows [1]. One group of chromogenic materials is comprised of photochromic compounds, which are characterized by the ability to change their optical properties reversibly when exposed to light, and thus can be used for the fabrication of windows with dynamic and situation-determined solar control properties [2]. Photochromic materials exist both in organic and inorganic varieties [3], where some inorganic examples include titanium oxide, tungsten oxide, molybdenum oxide and yttrium hydride [4].

The discovery of photochromic properties in yttrium hydride came as a result of the increased scientific activity [5–10] that followed the discovery of the switchable optical properties in yttrium and lanthanum-based hydrides [11]. First, photochromism in yttrium hydride was observed only at high hydrogen pressures (above 5 GPa) [12], but by incorporating oxygen into the material, Mongstad et al. [4] later showed that photochromic properties also could be obtained at ambient conditions.

The material in the latter study was named *oxygen-containing yttrium hydride* (YH_x:O), as it was experimentally shown to contain up to ~30 at% oxygen [13]. The oxygen in YH_x:O has earlier been reported to unintentionally get incorporated during the reactive sputter deposition process used for fabrication, where the low electro-negativity of yttrium was believed to cause a reaction with oxygen-containing impurities in the deposition chamber [4,13,14]. YH_x:O have been found to exhibit an *fcc* cubic structure similar to the one of YH_2 but with larger lattice parameter (~ 5.4 Å) [15]. Its band gap has been measured as ~3.0 eV, [14] making YH_x:O thin films very transparent in their clear state.

A recursive problem with the aforementioned reports on YH_x:O is that they fail to supply a definite explanation for how oxygen gets introduced into the material. It has been proposed that oxygen originate from impurities within the sputter deposition chamber used for fabrication, [4,13,14] but experimental observations have this far been found to contradict this claim. Films with various electronic properties, oxygen contents and optical appearances have for example been fabricated within the same deposition chamber with a constant impurity content, [4,13–17] hence suggesting that the source of oxygen might be a different one.

In this work, we report on a method for how to synthesise photochromic YH_x:O, while presenting a definite proof of the source of oxygen. The process consists of an initial reactive magnetron sputter

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http://dx.doi.org/10.1016/j.solmat.2017.02.001
Received 12 November 2016; Received in revised form 30 January 2017; Accepted 1 February 2017

Please cite this article as: Montero, J., Solar Energy Materials & Solar Cells (2017), http://dx.doi.org/10.1016/j.solmat.2017.02.001

deposition of oxygen free yttrium hydride films, followed by an exposure to air that ensured incorporation of oxygen into the material. All films were inspected optically and analysed using x-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDS) and x-ray photoelectron spectroscopy (XPS).

2. Experimental

Oxygen free yttrium hydride thin films (YH_x) of ~500 nm thickness were initially deposited on soda lime glass through sputtering of metallic yttrium in a hydrogen-containing atmosphere. A 99.99% pure metallic yttrium target was used and the sputter process was performed in a Leybold Optics sputter deposition unit operated with a power density of 1.33 W/cm^2. The base pressure in the chamber was $\sim 10^{-6}$ mbar and the deposition was performed at 10^{-2} mbar in an approximate 1:10 flux ratio of hydrogen (5N) and argon (5N). No oxygen was intentionally introduced in the deposition chamber. Prior to removal from the vacuum chamber, some YH_x films were capped with ~200 nm of aluminium. The sole purpose of this capping was to protect the yttrium hydride films from oxidation upon subsequent exposure to air. In order to minimize the possibility of any reaction with oxygen in the period between fabrication and characterization, these films were stored in sealed containers purged with nitrogen.

The aluminium capping was fabricated with a low but non-zero oxygen permeability. Thus upon exposing the combined film to air, the aluminium ensured a limited flow of oxygen to the YH_x that allowed for an *in-situ* study of the reaction that followed. The visual development of the films during the reaction was studied optically from the substrate side of the sample, while the crystal structure was monitored through periodic grazing incidence X-ray diffraction (GIXRD) measurements. In the latter, a measurement was performed every ~30 min employing a Bruker Siemens D5000 diffractometer, operated with a 2° grazing incidence angle of Cu-K_α radiation. The optical reflectance of the capped films was measured before and after the complete reaction and compared with that of a non-capped, reacted film. These measurements were conducted from the substrate side of the films and performed over the 300–1700 nm wavelength range, employing two Ocean Optics spectrophotometers (QE65000 and NIRQUEST512) equipped with an integrating sphere.

The aluminium capped YH_x thin films were characterized using a Hitachi S-4800 scanning electron microscope (SEM) mounted with a Thermo Noran energy dispersive x-ray spectroscope (EDS). Secondary electron imaging (SEI) was mainly used for investigation of the film integrity, while EDS was employed in order to obtain an estimate of the oxygen concentration in the yttrium hydride. In order to get a sufficient signal from the capped YH_x films, the acceleration voltage was kept at 15 keV during EDS-measurements. This enabled the beam to penetrate through the capping layer and generate a signal from the YH_x. Since hydrogen is not detectable with EDS, all oxygen concentrations (C_O[%]) are given relative to the concentration of yttrium only: $C_O[\%] = C_O/(C_O+C_Y)$.

X-ray photo-electron (XPS) measurements were performed using a PHI 5000 Versaprobe XPS unit in order to verify the oxygen concentrations obtained using EDS. In the case of the capped films, an analysis was performed both on as-deposited and on reacted films. This was done by sputtering with a 3 keV argon gun through the aluminium capping before a scan was executed. The uncapped samples were analysed after pre-sputtering of the surface.

3. Results and discussion

Upon immediate removal from the vacuum chamber, the aluminium capped YH_x films were observed to have a dark, opaque appearance (Fig. 1a). This differed from non-capped samples fabricated under the same conditions, which likely due to an instantaneous reaction with air, were observed to have a transparent, light yellow appearance (Fig. 1d).

After a few minutes of air exposure, however, the capped samples were observed to have begun undergoing a slight reaction. Small parts of the films were observed to acquire a yellowish discolouration (Fig. 1b), not different from the color of the non-capped films. Upon prolonged storage in air (~hours), this reaction spread across the respective films, eventually causing the entire film to transform (Fig. 1c). The reflectance of the films presented in Fig. 1a, c and d, is shown in Fig. 2. The reflectance data reported has been measured respect to a high Lambertian diffuse reflectance standard, manufactured by Spectralon (model SRS-99-010) with a 99% reflectance factor. The capped unreacted YH_x film (Fig. 2a) shows a high reflectance for long wavelengths, a property that indicates the presence of free charge carriers [18]. The lack of optical interferences in the reflectance implies that the unreacted film is optically very thick, i.e. very absorptive. However, the reflectance curve of the capped reacted film (Fig. 2b) resembles the curve of the uncapped film (Fig. 2c), that is, it exhibits interference fringes and a decrease of the reflection in the near infrared. These results suggest that the as-deposited material is of metallic origin, which upon reaction with air turns into a wide-band gap semiconductor.

The YH_x:O films are known to darken reversibly under UV and blue light, as well as under standard AM 1.5 solar illumination [4]. In the present work, the photochromic effect in an uncapped sample is illustrated in Fig. 2d, where the optical transmittance before (clear state) and after 1 h illumination with a 3 mV, 405 nm violet laser (photodarkened state) are shown. The change in the transmittance is reversible, as shown in Fig. 2e, where the average optical transmittance in the 500–800 nm range is depicted during 1 h illumination/2 h darkness cycles.

Investigations with SEM and EDS were performed in order to gain insight into the reaction observed in the capped samples. In the secondary electron (SE) micrograph in Fig. 3a, the combined film can be observed to have swollen and de-laminated in the areas to the left and right (Fig. 3c), while being fully intact in the central areas (Fig. 3d). By comparison with the visual appearance of the YH_x (similar to Fig. 1b), the swollen, de-laminated areas were found to coincide with the areas of the YH_x visually confirmed to have undergone a reaction. Upon investigation with EDS (a line scan from left to right - Fig. 3a,b), the C_O in the reacted areas was measured as ~40 at%, approaching the ~50% measured in uncapped samples. On the other hand, the non-reacted areas showed a C_O measuring ~5%, a value that can be explained by for example a surface oxidation of the aluminium capping itself, a contribution from the glass substrate, and/or impurities in the microscope chamber.

After argon gun sputtering through the capping layer, investigations with XPS showed a C_O in the non-reacted capped and reacted capped YH_x films measuring 18% at. and 64% at. respectively. The C_O in the pre-sputtered, non-capped, reacted YH_x was measured as 61% at., being similar to that found for the reacted capped sample. The relatively high concentration of oxygen found in the non-reacted capped sample can be explained by post-sputter oxidation of the topmost surface of the sample during the XPS measurement. Contaminants in the XPS chamber can adsorb on the surface of the now unprotected YH_x, yielding a significant signal in the surface sensitive XPS. This claim was proven by performing periodic measurements of the same sample which showed an increasing oxygen signal as a function of time. However, since the base pressure of the deposition chamber is 10^{-6} mbar, the possibility of a small fraction of oxygen being incorporated during the deposition process cannot be totally ruled out [4].

Investigation of the non-reacted, capped material (Fig. 1a) using GIXRD reveals an fcc crystal structure and a lattice parameter a=5.2 Å. The match between this and what has earlier been reported for yttrium di-hydride (YH_2) [19] leads to the suggestion that this as-deposited material is in fact YH_2, a claim is supported by the presented optical