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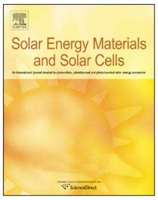

Dynamic reactive sputtering of photochromic yttrium hydride thin films

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ABSTRACT

For practical applications of the oxygen-containing yttrium hydride-based photochromic films, knowledge about deposition on substrates of different types and sizes is an important issue. In this article, we report on the dynamic reactive sputter deposition of the films on small and large-area glass and plastic substrates. By analysis of the optical properties we show that all the deposited films exhibited photochromic effect. Surface morphology and structural properties of the films have been studied.

1. Introduction

The increasing demand in using smart windows requires low cost and advanced chromogenic materials and devices. Electrochromic devices (ECD) are one of the most extensively studied smart windows and belong to the category of active windows with considerable commercial interest due to their controllable transmission, absorption and/or reflectance [1–6]. Advantage of the devices is that they can be controlled directly by humans or building automation systems. Due to the complexity of electrochromic systems and high price there is a renewed interest in the category called passive windows possessing thermochromic and photochromic properties. They respond to heat or ultraviolet (UV) light and can be used as, e.g., anti-UV coating blocking the UV light that causes skin wrinkles and sunburn. However, switching the optical properties of the passive windows cannot be controlled manually. For example, such windows can darken to control heat and UV light even when it is not wanted. In the winter time when heat and light might be needed to enter the building, the passive technologies do not offer the capability to prevent the tinting. Nevertheless, nowadays, such passive windows look quite attractive from the perspective of future technological development.

Several organic and inorganic materials as well as their hybrids have been reported [7] to possess photochromic properties such as, e.g., WO_3 [8–10], V_2O_5 [11], viologens [4], etc. Recently, a new material, O-containing YH_x [12] (YH:O), joined the family of photochromic materials. Upon illumination by UV and/or visible light, the material changes its optical properties from transparent to dark and has the potential to be used as anti-UV coating for windows. Some information is already available about deposition and properties of the material [13]. Compositional analysis has been performed and presence of large amount of oxygen is established [14]. Photo-induced reduction of work function has been reported [15]. X-ray photoelectron spectroscopic (XPS) measurements show [15] high levels of oxygen, which agrees with earlier findings [14]. It is suggested that the oxygen atoms in oxygen-containing transparent yttrium hydride bind to OH complexes which find their place in the H positions of theYH_2 lattice. Time-resolved X-ray diffraction (XRD) studies showed a photo-induced structural rearrangement leading to a lattice contraction [16], indicating that the mechanism underlying the photochromic reaction might be not purely electronic. By solid-state nuclear magnetic resonance (NMR) studies a model for the light-induced structural transformation of the films has been reported [17]. It is found that some of the hydrogen atoms are mobile, which will be diminished during the photochromic darkening, some of the yttrium species gets into a metallic state. Optoelectronic phase

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segregation of metallic entities in a dielectric matrix is suggested [18]. From analysis of optical properties it is found that substantial photodarkening of the films can be caused by photons of sub-band-gap energy [12,18]. Possibility of optical band gap engineering is established [19], which can be controlled by deposition pressure. In practical applications of the photochromic materials, knowledge of deposition on different type and size of substrates is an important issue. In this article, we report on the fabrication and characterization of YH:O thin films on small and large-area glass and plastic substrates.

2. Experimental details

Reactive deposition of the thin films of YH:O has been performed in the on-axis pulsed in-line DC magnetron sputtering machine produced by Leybold Optics A550V7. The DC power of 1000 W with a pulsed frequency of 70 kHz was applied to the Y target. 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 5 N and 6 N, respectively, were used. The films were grown at room temperature and in a mixed atmosphere of argon and hydrogen at a total pressure ranging from 0.4 to 6 Pa. The total gas flow of argon and hydrogen was kept constant at 200 sccm with an Ar:H_2 gas ratio of 4:1. The yttrium hydride thin films were deposited on glass substrates (Menzel-Gläser microscope slides with a thickness of 1 mm in dimensions of 26 mm × 76 mm) and commercial window glass (20 cm × 20 cm). The films have also been deposited on 13 × 13 cm^2 plastic mylar substrates. The nominal thickness of the flexible mylar sheet is 127 μm. In order to investigate the effect of substrate position on the resulting film composition and homogeneity, three glass substrates have been used. This corresponds to a deposition zone with width and length of 26 and 228 mm, respectively. 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 substrates were mounted on fixed positions on the carrier using commercial Kapton tape. The substrate carrier was operated either in stationary or oscillating (dynamic) deposition modes in the present study. Since the size of the substrate carrier is 740 mm × 660 mm, it offers possibility to produce thin films with similar dimensions. In addition, by carefully optimizing the sputtering conditions, high quality and uniform large-area samples can be reproducibly achieved.

The film thickness was determined using a stylus surface profilometer. Electrical resistivity of the samples was determined by a four-point probe setup. The optical properties of the thin films were characterized using an Ocean Optics QE65000 optical spectrometer. In order to induce the photochromic effect, thin films were illuminated for 1 h under artificial sunlight from a solar simulator with an intensity of 0.1 W/cm^2 at ambient conditions. The surface morphology of the thin films was examined by employing an atomic force microscope (AFM) from Surface Imaging Systems operated in non-contact mode. 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.

3. Results and discussions

Fig. 1(a–e) displays photographs of YH:O films deposited on glass substrates at pressures in the range of 0.4–6.0 Pa. The films were obtained when location of the carrier was fixed. The film thickness was ranging from 600 to 1300 nm. The growth rate of the films was found to decrease with increasing deposition pressure. Analysis of Fig. 1(a–e) shows that when the substrate position was varied with respect to the fixed Y-target, composition of the films will be non-uniform as we demonstrated it in deposition of Mg_2NiH_4 films [20]. Such non-uniformity is well defined in the films deposited at the pressure 0.4 Pa [Fig. 1(a)]. The film consists of two different regions, which are visually well seen. One is black and reflective and the other region is slight yellow and is partially transparent. In previous work [21], we have shown that the crystal structure of both black and semi-transparent regions of the YH:O films are crystallized into face-centered-cubic (*fcc*) lattice. Chemical composition was found to be close to YH_2 for the black and to YH_3 for the semi-transparent regions. Clearly, the semi-transparent region is more hydrogen-rich as compared with the black region. The electrical resistivity for the black and semi-transparent regions was measured to be $\sim 10^{-3}$ and $\sim 10^5$ Ω cm, respectively. This demonstrates that the black region of the film is metallic, whereas the transparent region is electrically insulating. Moreover, as the deposition pressure was increased to 1.2 Pa, i.e., more hydrogen and argon gases were introduced into the process chamber, the black and semi-transparent regions ceased to coexist. All three samples were found to be transparent, as displayed in Fig. 1(b). However, it can be seen that for stationary sputtering, there is an apparent compositional gradient along the horizontal direction of the films. We note that similar film growth behavior has also been observed previously for reactive magnetron co-sputtering of Mg_2NiH_x thin films [20]. Fig. 1(c–e) demonstrates that the optical appearance of the transparent thin films was gradually changed from yellowish to whitish as the deposition pressure was increased from 1 to 6 Pa. The dependence of optical properties on the deposition pressure is reported elsewhere [19].

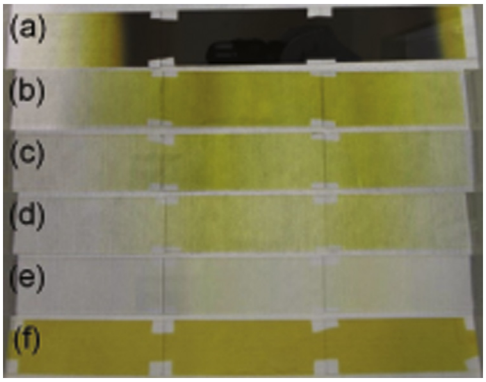

Fig. 1. Photographs of YH:O thin films deposited on glass substrates at total gas pressures of (a) 0.4, (b) 1.2, (c) 2, (d) 3 and (e) 6 Pa. The films were deposited using a stationary carrier. (f) Representative YH:O thin films obtained at a deposition pressure of 0.8 Pa by oscillating the substrate carrier in front of the Y target.

In order to produce uniform thin films, the impact of oscillating substrate carrier on the film deposition was investigated. Fig. 1(f) shows three representative 600-nm-thick films deposited by oscillating the substrate carrier 200 times in front of the Y target, with a carrier speed of 3 m/min and an oscillation width of 600 mm. The deposition pressure was 0.8 Pa. As can be seen, all samples deposited with oscillating substrate carrier appeared to be relatively homogeneous. It should be pointed out that completely black and conductive samples were grown when a deposition pressure of 0.4 Pa was applied. This finding suggests that high deposition pressures in combination with dynamic reactive sputtering are necessary for realizing large-area uniform thin films

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