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The electronic state of thin films of yttrium, yttrium hydrides and yttrium oxide

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ABSTRACT

Thin films of yttrium hydride have for almost 20 years been under investigation for optoelectronic and solar energy applications due to the hydrogen-induced switching in electronic state from the metallic elemental yttrium and yttrium dihydride to the transparent semiconductor material yttrium trihydride. In this study, we investigate the electronic structure of yttrium, yttrium hydride and yttrium oxide by using X-ray photoelectron spectroscopy and kelvin probe measurements. The investigated samples have been prepared by reactive sputtering deposition. We show that the electronic work function of transparent yttrium hydride is of 4.76 eV and that the recently discovered photochromic reaction lowers the electronic work function of the transparent hydride by 0.2 eV.

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1. Introduction

Thin films of yttrium hydride came into the light of attention with the invention of the metal hydride-based switchable window in 1996 [1]. The switchable window effect has later been subject for intense research and development, and has enabled a new class of smart windows and optical hydrogen sensors [2]. Yttrium hydride is generally considered to belong to the class of the rare-earth metal hydrides, for which the metal–hydrogen phase diagram is divided in three phases [3]; the metallic phase with dissolved small amounts of hydrogen is called the α-phase; the metallic dihydride (YH_2) is known as the β-phase; and the semiconducting trihydride (YH_3) is known as the γ-phase. YH_3 is a semiconductor with a band gap of 2.6 eV and therefore partly transparent to visible light [1]. Thin films of yttrium capped by a thin layer of Pd are gasochromic; H can be loaded and unloaded reversibly through the Pd cap layer and the optical state of the YH_x films can be controlled by regulating the H_2 pressure in the environment of the sample.

Recently we reported that thin films of yttrium hydride are not only gasochromic, but can also be photochromic: Films of reactively deposited transparent yttrium hydride exposed to light will gradually increase the optical absorption and the transparency will be reduced by up to 50% under illumination. The films will return to the initial

transparent state under relaxation in dark conditions [4]. This effect has so far only been visible in films prepared by reactive sputtering, where both hydrogen and oxygen are incorporated in the films during the process. The reactively deposited and oxygen-containing yttrium hydride films differ from hydrogenated yttrium films in the crystal structure; they have a cubic lattice similar to YH_2, whereas transparent YH_3 normally is found in a hexagonal structure [5,6]. The currently available results suggest that the photochromic effect is accompanied by a small structural change [7], but at the same time, changes in resistivity and the spectral response in relation to the band gap suggest that it originates from an electronic effect [8].

The electronic structure of yttrium hydride was first investigated experimentally by Fujimori and Schlapbach, who reported of a hydrogen-induced state at 6 eV in the valence band spectra. The Y 3d doublet core levels was found to shift by 0.7 eV and 1.2 eV, respectively, when going from pure Y to $YH_{2.1}$ and $YH_{2.1}$ to YH_3. More recently, shifts of 0.4 eV and 1.5 eV was reported by Hayoz et al. [9]. Dús and Nowicka [10] have investigated the dynamic changes in the work function of yttrium films upon hydrogen uptake, but we have not been able to find absolute values for the work function of yttrium hydride in the literature.

2. Experimental

Four different thin film samples were investigated in this work; elemental yttrium metal, black yttrium hydride (the YH_2 electronic

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state), transparent yttrium hydride (the YH$_3$ electronic state) and yttrium oxide (Y$_2$O$_3$). Thin films of yttrium and yttrium hydride were prepared by magnetron sputtering. The yttrium films were prepared by deposition from a metallic target in Ar atmosphere, whereas transparent and black metallic yttrium hydride films were prepared in a reactive atmosphere with Ar and H$_2$, as described elsewhere [5]. The yttrium oxide film was prepared by thermal oxidation of a metallic Y film. Optical transmission and X-ray diffraction measurements revealed no sign of metallic particles or phase separation in the hydride or oxide films. All the films were deposited on glass and had a thickness of 300–400 nm.

The samples were investigated by X-ray photoelectron spectroscopy (XPS) using a KRATOS AXIS ULTRA^{DLD} instrument with monochromatic Al Kα radiation ($h\nu = 1486.6$ eV) operated at 15 kV and 15 mA. The sample surface was sputtered prior to measurement to remove potentially oxidized surface layers. The spectra were peak fitted using the CASAXPS program after subtraction of a Shirley type background. The spectra were calibrated by using the C 1s peak before sputtering and Ar 2p peak (at 243.9 eV) after sputtering.

The work function of transparent yttrium hydride was measured using the Kelvin probe method [11], with a stainless steel vibrating probe with a 3.2 mm diameter disk. The measurement of the surface potential, and in particular the contact potential difference (CPD), over a large area gives comprehensive information about the homogeneity and uniformity of the surface. The surface topography is obtained by scanning measurements with a spatial resolution of 10 μm using a step motor driven X–Y translation stage with a hemispherical (0.5 mm diameter) stainless steel reference probe. The work function measurements are also carried on the transparent yttrium hydride thin films after illumination by sunlight for 1 h on a 2 mm × 2 mm spot, in order to observe any contrast in work function as a result of the photochromic activation.

The contact potential difference (CPD) measures the surface potential difference between the surface of the sample and the stainless steel vibrating reference electrode. The relation between the work function of the film: $\phi_{\text{thin film}}$ and the work function of the reference electrode φ_{ref} and the CPD is

$$e(CPD) = \phi_{\text{ref}} - \phi_{\text{thin film}}$$
$$= \phi_{\text{ref}} - [\chi + (E_c - E_f)_{\text{bulk}}] - \phi_{\text{ss}} \tag{1}$$

the change in the CPD are related to changes in the electron affinity χ, the band bending due to surface states ϕ_{ss} or a shift in the bulk Fermi level $(E_c - E_f)_{\text{bulk}}$. If χ remains constant, then the changes in CPD are directly related to the shift of the Fermi level in the bulk material and band bending due to the surface states. Any change in the Fermi level is due to the change in the electron or hole concentration, brought about by the incident sunlight in the present case. An increase in the CPD may directly be attributed to the enhanced electron concentration relative to the dark condition.

3. XPS spectra

Fig. 1 shows the collected XPS spectra for the four different films. The measured peaks have been fitted using the literature data for binding energy of the core levels of the compounds. Pure Y has a reported binding energy of 155.6 eV (3d$_{5/2}$) [9], while Y$_2$O$_3$ has a reported binding energy of 156.8 eV (3d$_{5/2}$) [12], a 1.2 eV chemical shift ($\Delta = EB$-$Y_{5/2}^{3+} - EB$-$Y_{5/2}^0$). The binding energy of the two peaks in the Y3d spectrum for the sample with mostly pure Y corresponds well to these two peaks. The pure Y peak has been fitted with a doublet separation of 2.06 eV, a Gaussian function with a small tail of GL(70)T(1) and with a FWHM of 0.5 eV. The O1s spectrum contains one small peak from Y$_2$O$_3$. The binding energies of the two peaks with the chemical shifts are presented in Table 1.

The Y3d spectrum from the oxidized Y sample has been fitted with two peaks. These peaks are found at a much higher binding energy than expected for both the Y$_2$O$_3$ and the Y(OH)$_x$ peak, as seen in Fig. 1. This large shift of the Y$_2$O$_3$ and the Y(OH)$_x$ peak has previously been described by Gougousi and Chen [13]. They explain that this shift is due to carbon and oxygen containing species such as carbonates and hydroxycarbonates, which are more electronegative elements resulting in an increased binding energy of the Y peaks. However, no carbon or extra oxygen peaks have been observed in our spectra. The peak shift may therefore be due to charge separation in the O–Y–H from O–Y to H, leaving Y–O to be more positive, therefore resulting in an increased binding energy. The binding energy found here for the Y$_2$O$_3$ peak is the same Otha et al. found in their work [11]. Fig. 1 shows the Y3d spectrum of the oxidized sample before (at the surface) and after Ar etching. The peak binding energies are the same, which shows that there is no reduction of the oxide due to Ar etching. Fig. 1 also shows the Y3d spectra of the YH$_x$ transparent sample at the surface and in "bulk" after Ar etching. The oxide peaks present in the sample at the surface have a 0.3 eV lower binding energy than found in "bulk" YH$_x$. It is expected that there is no hydrogen present in Y$_2$O$_3$ near the surface. However, in "bulk" YH$_x$ hydrogen may be attached to the oxide resulting in a larger charge separation which may lead to an increased binding energy. The increased binding energy could also be due to a change in coordination around Y$_2$O$_3$ by the introduction of areas of YH$_x$.
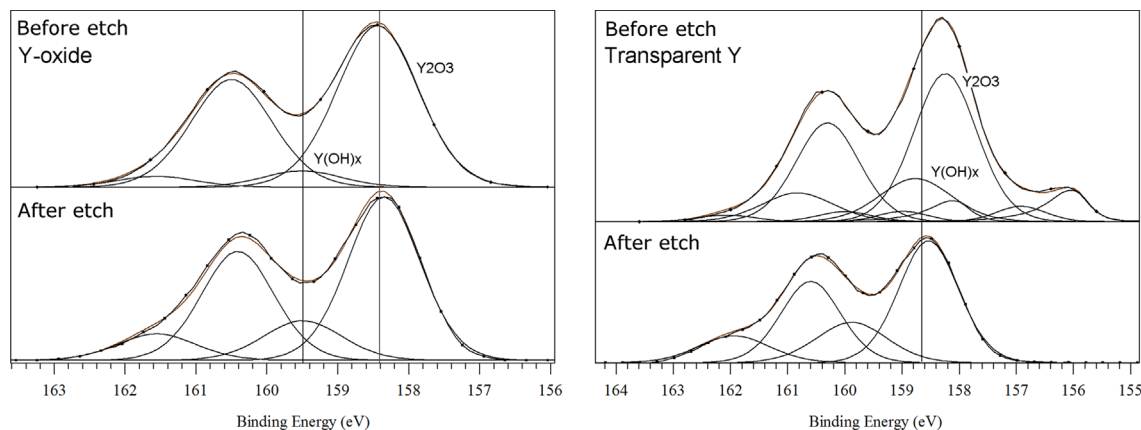

Fig. 1. Y-3d spectrum of the Y$_2$O$_3$ and YH$_x$-transparent sample before (at the surface) and after Ar etching.