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

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**Thin films of yttrium hydride have for almost twenty 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.**

## 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; the 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 is 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 suggests that it is 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.

## Experimental

Four different thin film samples were investigated in this work; elemental yttrium metal, black yttrium hydride (the $YH_2$ electronic state), transparent yttrium hydride (the $YH_3$ electronic state) and yttrium oxide ($Y_2O_3$). 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 (hv=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 hour 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: $\phi_{thinfilm}$ and the work function of the reference electrode $\phi_{ref}$ and the CPD is

$$e(CPD) = \phi_{ref} - \phi_{thinfilm}$$

$$= \phi_{ref} - \left[ \chi + (E_c - E_f)_{bulk} \right] - \phi_{ss} \qquad (1)$$

The change in the CPD are related to changes in the electron affinity $\chi$, the band bending due to surface states $\phi_{ss}$ or a shift in the bulk Fermi level $(E_c\text{-}E_f)_{bulk}$. If $\chi$ 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.

## XPS spectra

Figure 1 shows the collected XPS spectra for the four different films. The measured peaks have been fitted using 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 $Y_2O_3$ has a reported binding energy of 156.8 eV ($3d_{5/2}$) [12], a 1.2 eV chemical shift ($\Delta =$ EB-$Y^{3+}_{5/2}$ − EB-$Y^{0}_{5/2}$). 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 $Y_2O_3$. 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 $Y_2O_3$ and the $Y(OH)_x$ peak, as seen in Figure 1. This large shift of the $Y_2O_3$ 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 $Y_2O_3$ peak is the same Otha et al. found in their work [11]. Figure 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. Figure 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 the $Y_2O_3$ 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 the $Y_2O_3$ by the introduction of areas of $YH_x$ .

The XPS spectra of all of the samples are displayed in Figure 2. The spectra of both the transparent and black yttrium hydride samples have peaks that may be attributed to pure $Y(\alpha)$, $Y_2O_3$, and $Y(OH)_x$. The binding energies and corresponding chemical shifts are presented in Table 1. The black $YH_x$ sample has been fitted with three additional peaks. However, the peak with the largest binding energy, at 159.09 eV fits well with the $Y(OH)_x$ from the oxidized sample and the surface. The other two peaks are located at a binding energy of 156.11 eV and 157.45 eV. The peak at 156.11 eV, with only 0.14 eV chemical shift, is close to pure $Y(\alpha)$. The peak at 157.45 eV, with a chemical shift of 1.48 eV, seems to fit well with $YH_3(\gamma)$ from the reference spectrum of Fujimori et al. [14].

The transparent $YH_x$ sample has also been fitted with three additional peaks located at a binding energy of 155.86 eV, 156.41 eV, and 157.28 eV. The first peak at 155.86 eV, with a chemical shift of -0.11 eV, fits well with $Y(\alpha)$. The peak at 156.41 eV and 157.28 eV fits well with $YH_2(\beta)$ and $YH_3(\gamma)$ from the reference spectra. However, the $YH_2(\beta)$ reference spectrum does not have the $Y3d_{3/2}:Y3d_{5/2}$ ratio which is expected for Y3d peaks, which should be 2:3. This spectrum is probably composed of both $YH_2(\beta)$ and $YH_3(\gamma)$.

$YH_3(\gamma)$ is the transparent phase with a HCP ($HoD_3$ type) structure, while $YH_2(\beta)$ is the black phase with the FCC ($CaF_2$ type) structure. XRD measurements of our samples showed that both the transparent and black samples exhibit the FCC lattice, as described earlier [5]. Table 1 shows the percentage of yttrium components present in "bulk" sample, interpreted from the XPS results. It can be observed that the black $YH_x$ sample resemble more pure metallic $Y(\alpha)$, while the transparent sample resembles more the $YH_3(\gamma)$. From Figure 2, the oxygen content can be compared between the four samples, normalized at the background. The spectra show an increased oxygen content in the transparent sample compared to the black sample.

In order to distinguish the yttrium hydride peaks from the oxide peaks in the spectra, the oxide from the surface have been subtracted from the etched spectra in Figure 3. In addition, the reference spectra of Y, $YH_2$, and $YH_3$ from [14] is included as a comparison.

| Sample | $Y3d_{5/2}$ peak (± 0.1 eV) | $\Delta= Y^{peak}3d_{5/2} -Y^03d_{5/2}$ (± 0.12 eV) | Compound | % of total Y composition |
|---|---|---|---|---|
| **Elemental $Y^o$-ref** | 156.06 | 0 | $Y (\alpha)\ Y^03d_{5/2}$ | |
| **$YH_2$ –ref** | 156.53 | 0.47 | $YH_2(\beta)$ | |
| **$YH_3$ -ref** | 157.55 | 1.49 | $YH_3(\gamma)$ | |
| | | | | |
| **Elemental $Y^o$** | 155.97 | 0 | $Y(\alpha)$ | |
| **Black** | 156.11 | 0.14 | $Y(\alpha)$ | 69.7 |
| | 157.45 | 1.48 | $YH_3(\gamma)$ | 25.6 |
| | 159.09 | 3.12 | $Y(OH)_x$ | 4.8 |
| **Transparent** | 155.86 | -0.11 | $Y(\alpha)$ | 30.3 |
| | 156.41 | 0.44 | $YH_2(\beta)\ (+YH_3(\gamma))$ | 36.5 |
| | 157.28 | 1.31 | $YH_3(\gamma)$ | 33.2 |

*Table 1*: The Y3d$_{5/2}$ binding energy of the four samples of the peaks fitted to the spectra, in addition to the chemical shift  Δ= Y$^{peak}$3d$_{5/2}$-Y$^0$3d$_{5/2}$, and the possible compound.


**Valence band**

The metallic Y sample has high density of states (DOS) at the Fermi level. This is due to the (4d5s)$^3$ conduction band [14], and is a typical metallic behavior. The valence band spectrum of the yttrium hydride samples will have a hydrogen-induced band at 5.5 eV. The peak between 0 and 1 eV results from metallic Y, due to the Y 4d$^1$ conduction band. This shows that the black sample has more metallic character than the transparent sample. The peak at 6.5 eV in the valence band spectrum of the transparent sample seems to be composed of two peaks. One of the peaks corresponds to the oxygen peak, and the other peak seems to fit well with the hydrogen-induced band at 5.5 eV. From the valence band spectra, band gap information may be extracted. Figure 4 compares the valence band spectrum of the transparent and black YH$_x$ sample. The valence band results for the transparent film suggests a band gap of close to 4 eV, whereas earlier optical measurements [5] and other reports [6] suggest a band gap of 2.6 eV. The reason of this discrepancy is due to different state of oxidation of the measured sample. The shown valence band spectra are from the surface of the films, which are highly oxidized, as we have described earlier [15]. Oxygen incorporation in yttrium hydride increases the band gap gradually from 2.6 eV for the pure hydride to 5.5 eV for pure oxide, as also described similarly for gadolinium oxihydrides [16]. Therefore, the band gap at the surface will be higher than that of the bulk of the film, the latter subject to the measurement of the optical band gap.


# Work function in photochromic YHx

Kelvin probe measurements conducted in the ambient on a transparent sample of yttrium hydride showed a work function of 4.76 ± 0.01 eV of the material. The results were repeatable and uniform over a large area of the sample. The repeatability indicates the non- reactive nature of the yttrium hydride surface, probably due to a protecting oxide layer already formed prior to the Kelvin measurements.

Figure 5 shows the CPD  scan of the surface of the yttrium hydride with a photochromic darkened spot in the center. As may be seen, a spot size of 2 mm x 2 mm is exposed to sunlight for one hour; this sunlight (of intensity ~ 70 mW/cm$^2$) triggers a photochromic darkening of the sample.  The photochromic darkening reduces the electrical resistivity and increases the optical absorption [3]. Consequently, the enhancement of photo generated carriers brings up the Fermi level towards the conduction band as shown by the change in the CPD values. While the illumination is incident on the sample, the charge generation gives raise to the quasi-static movement of Fermi level.  It may be shown from basic semiconductor physics [17] that the excess carrier density $n_{ex}$ due to illumination is related to the change in the work function:

$$n_{ex} = n_0^* - n_0 = 2 \left(\frac{2\pi m_e^* kT}{n^2}\right)^{3/2} \left[e^{\frac{2\phi^* - \chi}{kT}} - e^{\frac{2\phi - \chi}{kT}}\right] = 2 \left(\frac{2\pi m_e^* kT}{n^2}\right)^{3/2} e^{\frac{\phi^* - \chi}{\phi - \chi}} \qquad (2)$$

Here, $n_0$ is the carrier density of the sample, $m_e$ is the effective electron mass, $k$ is Boltzmann's constant, $T$ is the temperature, $\Phi$ is the work function and $\chi$ is the electron affinity, for which * demarcates the exited state. It may also be observed that the change in the CPD (equivalently, the enhancement of electron concentration) is spread over the edges and maximum at the center of the illumination.

The change in CPD corresponds to a change in the work function from 4.76 eV for the unexposed sample to 4.58 eV for the area exposed to sunlight. The change in the work function due to illumination is 0.18 eV: this is the value the Fermi level has gone up towards the conduction band, neglecting the change in the surface charge density due to illumination.

## Conclusion

The XPS spectra highlight the differences in the electronic state of the thin film samples of metallic Y, black yttrium hydride, transparent yttrium hydride and yttrium oxide. All spectra show presence of oxygen. Especially the reactively deposited yttrium hydride samples show high levels of oxygen, which agrees with earlier findings of high oxygen content in this kind of sample. However, as the optical properties resemble those of pure yttrium hydride and the structure is that of the common β-phase of yttrium hydride, it is still considered right to refer to these materials as yttrium hydrides. In the end it seems probable that the oxygen atoms in oxygen-containing transparent yttrium hydride bind to OH complexes which find their place in the H positions of the $YH_2$ lattice. Further information about the O positions could be obtained by performing an EXAFS investigation of the compound. Valence band spectra show a peak in density of states at the Fermi level for the black film, whereas transparent yttrium hydride has no such peak at the Fermi level. This is in agreement with the respectively metallic and insulating nature of the two materials.

Kelvin probe measurements give a value for the work function of 4.76 eV for transparent yttrium hydride. Knowledge of the work function is useful for construction of electrical or chemical devices that depend on the transport of electrons and ions between chemically and electronically different layers. We also show that the exposure of sunlight changes the electronic work function with almost 0.2 eV, corresponding to an increase in the free electron density and a lifting of the Fermi level towards the conduction band.

## Acknowledgements

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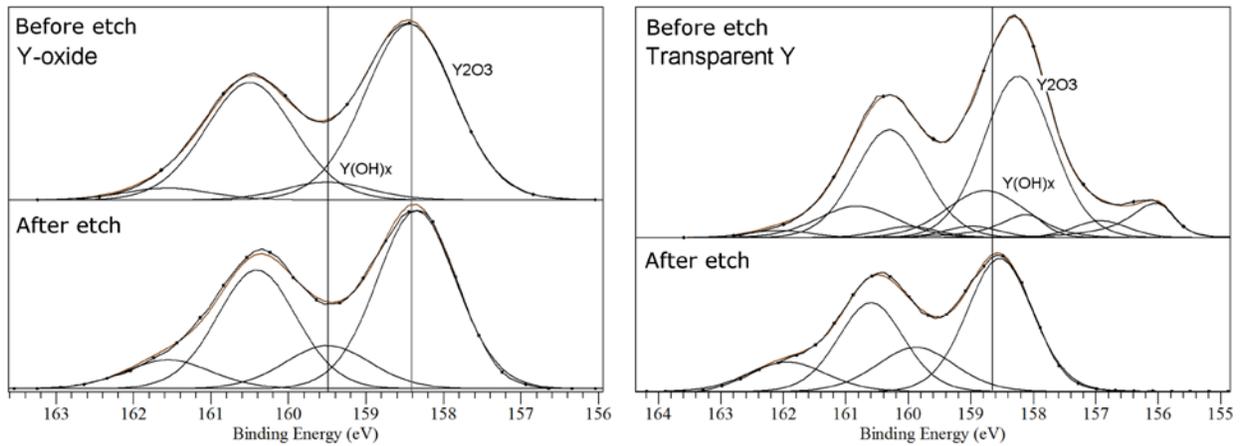
**Figure captions**



Figure 1: Y-3d spectrum of the $Y_2O_3$ and $YH_x$-transparent sample before (at the surface) and after Ar etching.
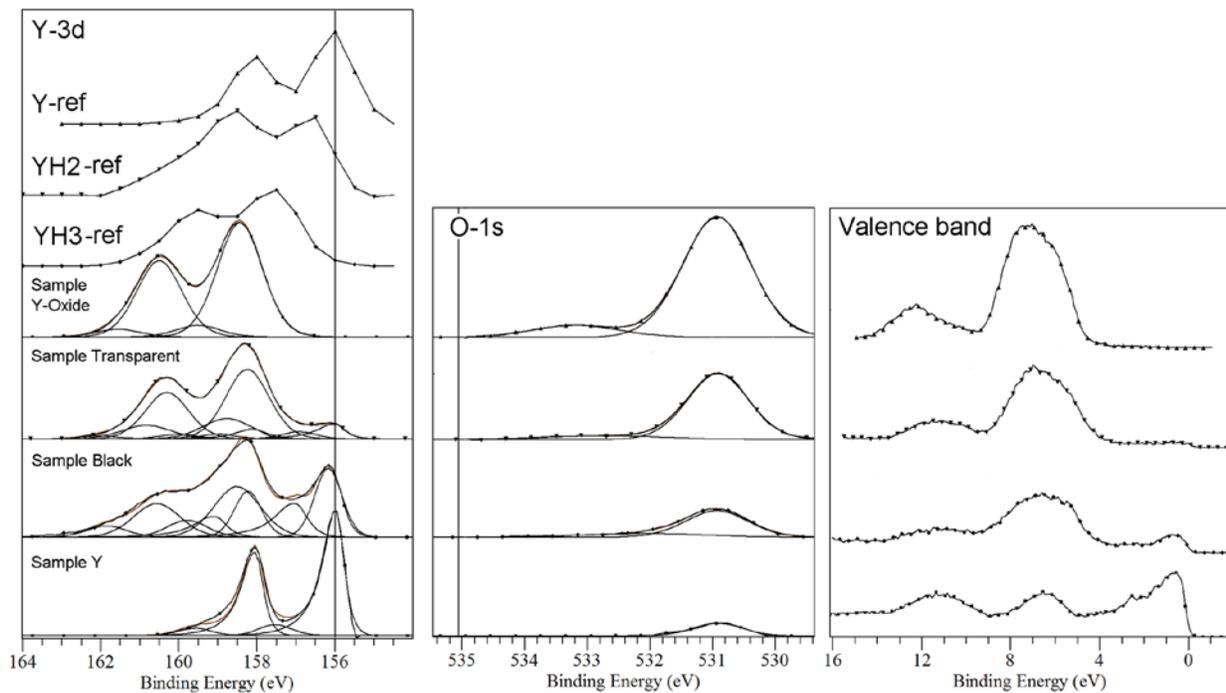


Figure 2: XPS spectra showing the Y-3d and O-1s core level binding energies and the valence band for elemental Y, black yttrium hydride, transparent yttrium hydride and an yttrium oxide film. In addition, the reference spectra of Y, $YH_2$, and $YH_3$ from [14] is included as a comparison.
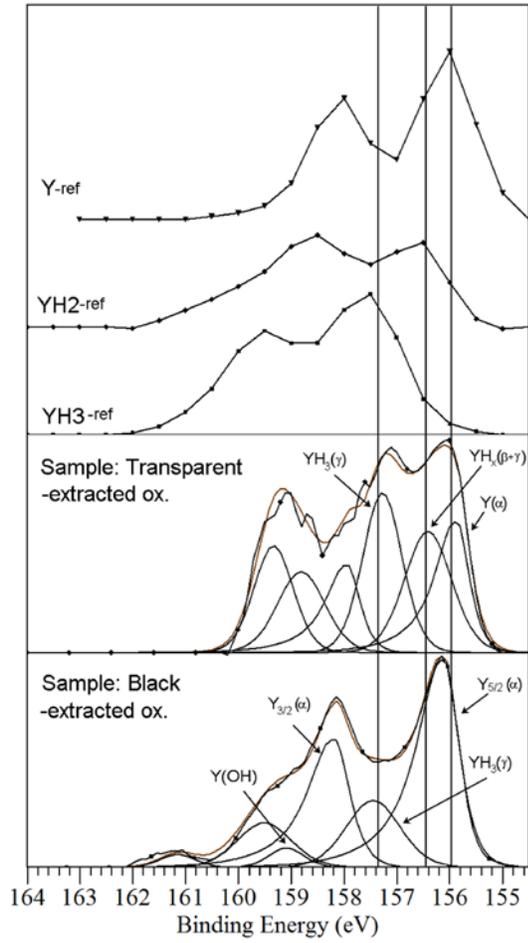
Figure 3: XPS spectrum of the transparent and black YH$_x$ samples after a subtraction of the oxide from the surface of the corresponding un-etched sample.

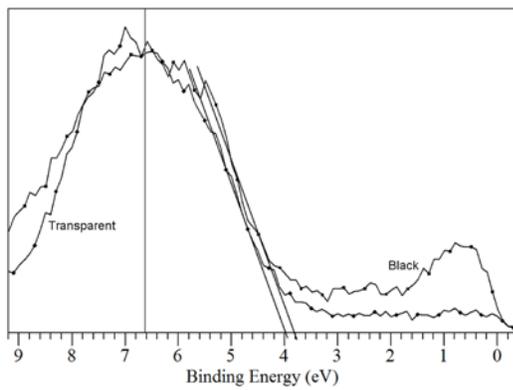

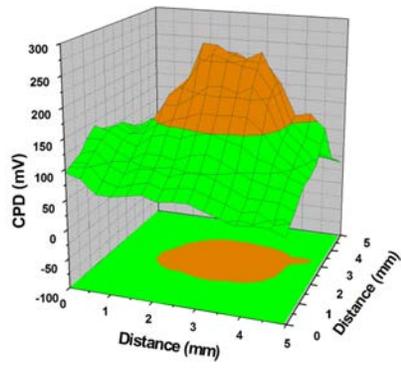Figure 4: Valence band of the black and transparent YHx samples.

Figure 5: Kelvin probe mapping results of the sample after exposure to sunlight on a spot on the sample.