ABSTRACT

In this project, I investigate the photoconductive nature of photochromic rare-earth metal oxy hydrides (REMHO). Such materials have received increasing scientific attention since they show a color-neutral photochromic effect that can be applied, e.g., in smart windows or chromogenic devices. Photochromic materials reversibly turn opaque from transparent under illumination with light of optical wavelength. In recent studies it was found that these materials also show an instant decrease in resistivity when illuminated which can be used in optical sensors. To understand the nature of this photoconductive effect, I grew yttrium oxy hydride thin films by reactive magnetron sputtering. I measured the resistivity for illumination from front and substrate side, optical transmission and compositions of the samples and related the results to photoconductivity. I show that photoconductivity is a bulk effect and not directly related to photochromism. Samples that almost lost photochromism due to aging, still show strong photoconductivity. Moreover, it was observed that the resistance increased faster during bleaching for front illumination than for back illumination.

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1 Overview

Photochromism denotes the electromagnetic radiation induced reversible change of optical transmission. The change of optical transmission goes back to its initial state when the irradiation is removed. This unique property can be applied to develop smart windows [1], optical switches, medical devices [2], optical data storage system and other photochromic devices. [1]

Rare-earth Metal hydrides have been studied after the discovery of their switchable optical properties at high pressure. [3] Oxygen containing yttrium hydride exhibiting optical switching at ambient temperature and pressure was reported in 2011 for the first time. [4] Later it was established that during the oxidation process, hydrogen is replaced by oxygen and the concentration of H and O in the film controls the photochromic property. [2] After this finding, O-containing hydride films were called oxy hydrides in which oxide and hydride anions are located in the same phase. [2]

In a more recent study, it was shown that under illumination, such REMHO (REM denotes rare earth metal) films change their electrical properties as well by showing sharp decrease in resistivity. [4] Photochromism associated with photoconductivity was first reported way earlier in 2001, however, at extremely low temperature [5] and again after 6 years at extreme hydrogen pressure and high intensity light, which makes the materials challenging for applications. [3] The actual reason behind this phenomenon is still not fully understood and more research is needed in order to reveal the underlying physics and enable their future applications. Many works correlate the photochromism with the composition of the REMHO thin films. [2,6,7] In Ref. [8], the resistivity of YHO was studied for samples with different compositions and it was concluded that the resistivity of the material decreases with decreasing oxygen concentration, which can be explained by the widening of band gap with increasing oxygen concentration. [4] Engineering the bandgap by changing the oxygen concentration and other factors allows to tune the photoconductive response for promising applications, as for example in photo sensors.

In this project, I combined results of compositional, optical, and electrical transport measurements performed on identical samples grown under same growth conditions. The resistivity measurement was done for front side illumination and illumination from the substrate side as well to see whether photoconductivity is connected to a bulk or surface effect. I grew 4 identical samples in every deposition run and used one sample from the batch for one measurement in order to avoid memory effects from previous measurements.

This report is structured in the following manner. In the next chapter, I described some background physics to explain the interaction of light with matter which is important to understand photochromism. Chapter 3 contains the description of the sample synthesis. The setup and process of optical and electrical measurements are presented in chapter 4 and 5, respectively. The results from all the measurements are outlined in chapter 6. In the 7th chapter, I discuss the aging effect on photochromism and photoconductivity. Correlation between these two phenomena is delineated in chapter 8. Finally, summary the findings of this project and suggested further works are provided in chapter 9 and 10, respectively.
2 Physics Behind Photoconductivity and Photochromism

In solid state physics, the physical properties of solids, such as photon absorption or electrical resistivity are explained with the help of band theory. In band theory, metals, semiconductors, and insulators are distinguished by the band gap between the valence and the conduction band and the position of the Fermi level. Band gap is the forbidden region between the valence and conduction band where no electron states can exist, and Fermi level is the highest occupied energy level at absolute zero temperature. In metals, there is no band gap due to an overlap of the valence and the conduction band. In contrast, a large band gap exists in insulators. In semiconductors, band gap is small enough for electrons to bridge the gap by thermal, electric or photon excitation.

Metallic yttrium transforms into yttrium hydride under hydrogenation which after exposing to oxygen, turns into a polycrystalline semiconductor with direct band gap of about 2.6 eV. [1] The electrons in the valence band of semiconductors can be excited to the conduction band by illuminating with light of visible wavelength. This increases the conductivity of the material which is denoted as photoconductivity. This phenomenon is not seen in metals or insulators since the band gap of insulators is larger than the energy of optical photon. On the other hand, metals have overlapping valence and conduction bands with zero band gap. For this reason, the conductivity of metal does not increase by exposing it to light. The main source of electrical resistance in a metal is the electron-phonon interaction.

Fig. 1 illustrates the band gaps in metal, semiconductor, and insulator and shows electron transfer due to photon absorption in semiconductors.

![Energy level diagrams in metal, semiconductor, and insulator](image)

*Fig.1: Energy level diagrams in metal, semiconductor, and insulator (taken from Ref. [9] and modified)*

The mechanism behind photochromism in oxygen containing rare earth metals is still unclear. [10] There have been a lot of studies done to understand and control the photochromic effect. It is known that the photochromic property can be tuned by engineering the band gaps of the materials. [11] In some photochromic materials, such as silver halide doped glasses, it is reported that the reversible formation of plasmonic nanoparticles gives rise to photochromism. [1] Ref. [12] reports an evidence for dual-phase formation in REMHO thin films and hypothesizes that hydrogen transfer between these two phases can be the reason of photochromic response. On the other hand, another study in Ref. [10], it proposed that the photodarkening originates due to the formation of small metallic opaque domains inside the material.
As photoconductivity is related to the transfer of electrons from the valence band to the conduction band by the absorption of light and this absorption may trigger a photochromic effect, the question arises whether the two phenomena are connected to each other.

3 Sample Preparation

In this project, I characterized the samples with respect to their optical and transport properties as well as chemical composition. The resistivity measurements were done in two ways: a) illumination from the front side and b) illumination from the back of the sample. Thus, four measurements had to be done on each sample. To avoid the impact of other measurements (memory effects), I grew 4 identical samples in every deposition run. Each batch of four samples was grown at the same time under same growth condition on glass substrates (microscopic slides) having high transmittance for visible light and high resistance. The glass slides were cleaned with iso-propanol and deionized water and then cut into small pieces each of about 1.4 cm*1.3 cm*1mm in dimension prior to film deposition.

Fig. 2a shows the four glass slides loaded at the same time into the sputter chamber. After deposition, the yellowish rare earth film is visible in Fig. 2b.

![Fig. 2: Quadruplet samples mounted on sample holder inside the deposition chamber: glass substrates before sputtering (left) and after thin film deposition (right).](image)

3.1 Thin Film Deposition by Magnetron Sputtering

Photochromic thin films were deposited by reactive magnetron sputtering. More details about the method can be found in Ref. [13,14]. This method is commonly used for depositing compound films from a target of a specific element. I used a 99.9% pure bulk Yttrium disc as target having 54 mm of diameter and 1 mm of thickness. In the method of direct current (DC) magnetron sputtering, energetic ions emitted from plasma, bombard the Y target. In reactive sputtering, a small amount of reactive gas is injected which in our case is H₂. A needle valve was used to control the gas flow. Yttrium is sputtered from the target in the presence of Ar and H₂ and forms a YH₂ thin film on the substrate. This yttrium hydride film is later
oxidized in air. Changing the sputtering time, distance between target and substrate, the Ar:H ratio in the chamber or the post oxidation time, YHO samples with different thickness or composition of O and H were prepared.

In this work, a compact Balzer Union sputtering system was used which consist of a cylindrical glass chamber, needle valve gas inlet, rough and high vacuum control unit, high voltage supply, etc. The cylindrical glass chamber of the sputtering device consists of water-cooled target arm, symmetrical magnet system that deflects the electrons and a shutter for pre-sputtering. The pumping speed of the rotary pump is $1.5 \text{ m}^3/\text{h}$ which results in a pressure $< 6.6 \times 10^{-3} \text{mbar}$. Higher vacuum is achieved by a turbomolecular pump (pumping speed for air: 50 l/s). In this work, the base pressures in the system were between $4 \times 10^{-5} \text{ mbar}$ to $8 \times 10^{-5} \text{ mbar}$.

Fig. 3 shows photographs of the setup of the compact magnetron sputtering device in the Tandem Laboratory, Uppsala University. Fig. 3a shows the Balzer Union magnetron sputtering device with plasma thawed in the cylindrical sputtering chamber. The backing vacuum pump is visible in Fig. 3b.

![Fig. 3: (a) Balzer Union magnetron sputtering device and b) Pfeiffer dual stage rotary vane vacuum pump.](image)

3.2 Parameter Optimization for Magnetron Sputtering

Five batches of calibration samples were grown under different growth conditions (such as target distance, base pressure, hydrogen flow, growth pressure and current) to find which combination of the parameters gives the best output i.e., evenly deposited thin film with maximum photochromic response. The target distance was 5 cm for first 2 batches and 6 cm for other batches. Base pressures and growth pressures were varied between $4 \times 10^{-5} \text{ mbar}$ to $8 \times 10^{-5} \text{ mbar}$ and $6 \times 10^{-5} \text{ mbar}$ to $10 \times 10^{-5} \text{ mbar}$, respectively. 20 sccm of hydrogen flow and 120 mA of current was maintained for all batches, except for SKY5, hydrogen flow was 16 sccm. Among all the samples, SKY3 appeared to be uniformly transparent with no gradient visible. I chose SKY3 from the calibration samples to produce a thickness series. 3 more batches of samples were grown with the same growth conditions as SKY3 which are 6 cm of target distance, $8 \times 10^{-5}$ of growth pressure and 20 sccm of hydrogen flow. This time I varied the sputtering
time (15 min, 10 min, 5 min) to get films of various thickness. The growth conditions and visual appearances of all samples are summarized in Table 1.

Fig. 4 shows the photograph of all samples grown in this project. Samples in 2 out of 8 batches were opaque. All other samples were transparent but with different colors. Variation in sample colors can be the result of the variation in film thickness as suggested in Ref. [7]

### Table 1: Growth parameters of the samples.

<table>
<thead>
<tr>
<th>#</th>
<th>Target distance, cm</th>
<th>Base Pressure, 10^{-5} mbar</th>
<th>Hydrogen Flow, sccm</th>
<th>Growth Pressure, 10^{-5} mbar</th>
<th>Current, mA</th>
<th>Growth Time, sec</th>
<th>Transparency/color</th>
<th>Date of deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>SKY1</td>
<td>5</td>
<td>8</td>
<td>20</td>
<td>9</td>
<td></td>
<td>1800</td>
<td>Initially black; transparent after 2 days</td>
<td>2020-11-20</td>
</tr>
<tr>
<td>SKY2</td>
<td>5</td>
<td>4</td>
<td>20</td>
<td>10</td>
<td></td>
<td>1800</td>
<td>Opaque (black)</td>
<td>2020-11-20</td>
</tr>
<tr>
<td>SKY3*</td>
<td>6</td>
<td>5</td>
<td>20</td>
<td>8</td>
<td>120</td>
<td>1800</td>
<td>Transparent (Yellowish)</td>
<td>2020-11-23</td>
</tr>
<tr>
<td>SKY4</td>
<td>6</td>
<td>6</td>
<td>20</td>
<td>6</td>
<td></td>
<td>1200</td>
<td>Opaque (black)</td>
<td>2020-11-23</td>
</tr>
<tr>
<td>SKY5</td>
<td>6</td>
<td>6</td>
<td>16</td>
<td>8</td>
<td></td>
<td>1800</td>
<td>Transparent (Yellowish)</td>
<td>2020-11-30</td>
</tr>
<tr>
<td>SKY6*</td>
<td>6</td>
<td>4.5</td>
<td>20</td>
<td>8</td>
<td></td>
<td>900</td>
<td>Transparent (Greenish)</td>
<td>2020-12-16</td>
</tr>
<tr>
<td>SKY7*</td>
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<td>4.5</td>
<td>20</td>
<td>8</td>
<td></td>
<td>300</td>
<td>Transparent (Pinkish)</td>
<td>2020-12-17</td>
</tr>
<tr>
<td>SKY8*</td>
<td>6</td>
<td>4.5</td>
<td>20</td>
<td>8</td>
<td></td>
<td>600</td>
<td>Transparent (Blueish)</td>
<td>2020-12-18</td>
</tr>
</tbody>
</table>

*Samples for the thickness series

![Image of samples](image)

**Fig. 4: Picture of all samples grown during this project.**

### 3.3 Verifying Chemical Composition and Thickness

The chemical composition and areal density of the samples were measured using two Ion Beam Analysis (IBA) methods: 1) Time of flight-energy elastic recoil detection analysis (ToF-E ERDA) and 2) Rutherford
backscattering spectrometry (RBS). ToF-E ERDA and RBS measurements were performed with 36 MeV \( I^{8+} \)
and 2 MeV \( He^+ \) beam, respectively. More details about using these techniques for characterizing the
composition of YHO samples can be found in Ref. [2,6].

In Table 2, the results obtained from IBA are summarized. The time when the measurement was taken
after the sputtering is given as well. The areal density was extracted from the RBS method from which I
calculated the thickness using the atomic density of YHO, \( R = (6.44 \pm 0.09) \times 10^{22} \text{at/cm}^3 \) obtained
from Ref. [7]. Exemplary graphs with data from ToF-E ERDA and RBS used for Table 2 can be found in Fig.
19 and Fig. 20 in the Appendix. The data from ToF-E ERDA and RBS measurements was analyzed using the
software named POTKU and SimNRA, respectively.

Table 2: Thickness, compositions, and oxygen concentration, \( \delta \) (oxygen to yttrium ratio) extracted from
IBA methods.

<table>
<thead>
<tr>
<th>#</th>
<th>Aerial Density, ( 10^{15} \text{at/cm}^2 )</th>
<th>Thickness (nm)</th>
<th>ToF-ERDA</th>
<th>RBS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Composition</td>
<td>Sample age during measurement (days)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H  O  Y</td>
<td>( \delta )</td>
</tr>
<tr>
<td>SKY3</td>
<td>6460</td>
<td>1003.1</td>
<td>36.1% 26.5% 37.4%</td>
<td>0.71</td>
</tr>
<tr>
<td>SKY6</td>
<td>2850</td>
<td>442.5</td>
<td>31.7% 29.1% 39.3%</td>
<td>0.74</td>
</tr>
<tr>
<td>SKY8</td>
<td>1860</td>
<td>288.8</td>
<td>25.4% 32.9% 41.7%</td>
<td>0.79</td>
</tr>
<tr>
<td>SKY7</td>
<td>870</td>
<td>135.1</td>
<td>16% 42.6% 41.4%</td>
<td>1.02</td>
</tr>
</tbody>
</table>

4 Measuring Optical Transmission of the Films

The photochromic response of the samples was examined by measuring the optical transmission before
and after the illumination using a UV-vis spectrometer. The schematic diagram of the optical setup is
illustrated in Fig. 5. The main two components of the optical measurement setup are the compact
stabilized tungsten halogen light source and the spectrometer (Kvant spectra-1). Other optical
components are two lenses (both having 12.5 cm focal length) for collimating the beam, neutral density
filter, sample holder, and aperture. At first, all the components were placed and aligned. A sample was
placed on the holder and transmission data was recorded. The sample is then illuminated for 5 minutes
with a deep blue light source with a power of 19.5 W and a wavelength of 455 nm. After 5 minutes of
illumination, the darkened sample was immediately placed on the sample holder of the optical setup and
the transmission data during bleaching was saved each 30 seconds over a period of 5 minutes. Later, the
transmission data was averaged over 450 nm and 800 nm range. The resulting transmission data are
plotted in Fig. 9a.
5 Measuring Electrical Transport of the Films

The two-point probe method was used for measuring the resistivity as our samples have high resistances ($\sim 10^{14}$ ohm to $10^8$ ohm). The four-point probe method works better for low resistance measurements as in this case the contact resistance is of higher relevance. The experimental setup was developed by Felix T. and the details are described in Ref. [8]. The setup consists of a 3D printed black box, plastic support with two probing points, the same deep blue light used in the optical measurement (with a power of 19.5 W and a wavelength of 455 nm), two fans for cooling, and switches to control the lamp and fans. The probes were connected to the HP 4339B high resistance meter allowing precision high resistance measurements. It can measure a wide range of resistance from $10^3$ ohm to $1.6 \times 10^{16}$ ohm with a sampling rate of 10 ms.

The resistance meter is connected to a computer equipped with a LabVIEW Virtual Instrument (VI) program to automatically save the results of the measurement (see Fig. 7). The source voltage is controlled by the LabVIEW Virtual Instrument (VI) as well. Current is measured for the applied voltage which gives the resistance following Ohm’s law and the data is saved in a file for further processing.

Fig. 6a illustrates a schematic diagram of the two-point probe method that has been used to measure the resistance of the films. Fig. 6b shows a picture of the resistivity measurement setup with resistance meter, lamp installed in the black box, fans and the LabVIEW virtual instrument. Fig. 7 is an image of the front panel of the virtual instrument used to record the resistance of the sample.
Fig. 6: (a) Schematic diagram of the two-point probe measurement (taken from Ref. [8]), (b) Resistance measurement setup with all components.

Fig. 7: Front panel of the LabVIEW virtual instrument.

One sample from the 4 identical samples was placed inside the plastic support (sample holder) and put inside the black box keeping thin film face up (Fig. 8a). The resistivity measurement was started, and the source voltage and measurement time was controlled from the VI. The blue light was switched on and the sample was illuminated for 5 minutes. After 5 minutes, the light was turned off and the resistivity during bleaching was recorded for additional 5 minutes. Another sample from the quadruplets oh the same batch was measured in the same way but this time the sample was illuminated from substrate side by putting the plastic support upside down in the box (Fig. 8b).
Fig. 8: Plastic support with sample attached inside, placed in the black box keeping sample face (a) up and (b) down during front and back illumination, respectively. The probing points and light beam path have been shown in the pictures.

6 Results

This chapter consists of two sections discussing the results obtained from the optical measurements (in the first section) and the resistivity measurements (in the second section) performed on the samples.

6.1 Photochromic Response

In Fig. 9, the average transmittance is plotted versus time before 5 minutes of illumination and during 5 minutes of bleaching illumination which is normalized w.r.t the transmission without sample. Among SKY6, SKY8 and SKY7, the thicker samples are less transparent before illumination compared to the thinner ones and showed stronger photochromism in accordance with Ref.[7]. However, the photochromic response measured after 5 minutes illumination for SKY6 is more than SKY3 which can be because of the aging of SKY3. SKY3 was 29 days old during the optical measurement whereas other samples were less than 1 week old. SKY7 (the thinnest sample) did not show any bleaching. The thinner samples quickly oxidize and are not photochromic for this reason. For the thick ones, the effect may saturate as the transmittance gets lower and the light is not able to reach deep enough into the film.

In Fig. 9b, we tabulate the photochromic response of the samples defined as the relative change in optical transmittance before and after the illumination.
In this section, I discuss different aspects of the results found from the resistivity measurement done on the samples. First, I have reported how different contacting points and temperature affected the resistivity measurement and what measures were taken to avoid these effects. Next, I show the difference of the photoconductive response due to illumination from front side and back side. In the end of this section, the thickness dependence of the photoconductive behavior of the samples are presented.

### 6.2.1 Effect of Different Contacting Points and Temperature

The results from the electric transport measurement on SKY3 showed that the measurement is affected by two factors:

- **Contacting points (see Fig. 10):** As I used a two-point probe to measure resistance, the contact resistance is not eliminated and affects the resistivity measurement.
- **Temperature:** The strong blue light used to illuminate the samples heats the sample and resulted in an increase of resistance (see Fig. 11(a)).

Fig. 10 depicts that the initial resistance of the same sample (SKY3) is different for 3 different pairs of the contacting points. To eliminate the effect of different contacting points, the data of resistance was normalized with respect to its initial value (Fig. 12) to allow a comparison of the time dependence of the resistance for front and back illumination irrespective of the initial value of resistance.
Fig. 10: Resistance of the same sample (SKY3) showing different initial resistances for 3 different pairs of the contacting points.

Fig. 11a shows the temperature effect during the resistivity measurement of SKY3. The resistance of SKY3 was recorded during 10 minutes of illumination followed by 10 minutes of bleaching. The resistance of the sample sharply decreased as the illumination started and kept decreasing slowly but after 5 minutes, the resistance started to increase even though the sample was still exposed to the blue light. As soon as the lamp was switched off (after 10 minutes), the resistance increased immediately as bleaching started. It turned out that the slight increase in resistance after 5 minutes of illumination was related to heating of the samples due to the intense light. To remedy this effect, an additional fan was installed during the resistance measurement of SKY5. This time resistance kept decreasing throughout the whole illumination period as seen in Fig. 11b.

Fig. 11: The evolution of resistance during and after illumination a) without additional fan, inset shows that the resistance started to increase after 5 minutes of illumination, b) after using additional fan, inset shows continuously decreasing curve of resistance.
6.2.2 Comparing Photoconductivity due to Front and Back Illumination

Fig. 12 presents the data from the resistivity measurement for illumination from substrate side (back illumination) and illumination from sample side (front illumination) of two identical samples taken from the SKY3 batch. The resistance of the samples sharply decreased as soon as they are exposed to the intense blue light continues decreasing slowly over the whole observation time. The illumination for 5 minutes leads to a decrease of resistance down to 0.1%-1% of its initial value. This decrease is reversible once the illumination is removed. Our data shows that after the illumination is stopped, the resistance increases slower for illumination from back compared to illumination from front side.

![Graph showing the resistance of SKY3 normalized with respect to the initial resistance during 5 minutes of illumination from front (black line) and back (red line) followed by 5 minutes of bleaching.]

**Fig. 12: Resistance of SKY3 normalized w.r.t the initial resistance during 5 minutes of illumination from front (black line) and back (red line) followed by 5 minutes of bleaching.**

6.2.3 Thickness Dependence of Photoconductivity

In the thickness series, SKY3 is the thickest sample followed by SKY6, SKY8 and SKY7 in sequence (the exact thicknesses are 1003.1 nm, 442.5 nm, 288.8 nm, and 135 nm respectively as listed in table 2). In Fig. 13, the evolution of resistance of all samples from thickness series during 5 min of illumination followed by 5 min of bleaching is shown. We see that the thinner the samples are, the more noise they show in the resistance measurement. Thicker samples show higher decrease in resistance due to illumination.
Fig. 13: Resistance of the samples of different thicknesses a) SKY3, b) SKY6, c) SKY8, and d) SKY7 normalized w.r.t the initial resistance during 5 minutes of illumination from front (black line) and back (red line) followed by 5 minutes of bleaching.

In Fig. 14, I have plotted photoconductivity with respect to thickness. Here, photoconductivity is denoted as the relative change of resistance before and after 5 min of illumination calculated from the plots in Fig. 13. The graph depicts that thicker samples show more photoconductive response compared to the thinner ones giving an indication that photoconductivity is a bulk effect. Moreover, we observe a saturation of photoconductivity above film thickness around 500 nm. This saturation can occur because of the transmittance getting lower for the thick ones and the light is not able to reach deep enough into the film. In Ref. [7], Moldarev et al. found that photochromic properties saturate for films thicker than ~ 600 nm, which is consistent with the results on photoconductivity in Fig. 14. Note, the thickest sample (SKY3) was 17 days old during the resistivity measurement whereas other samples were less than 1 week old.
8 Aging Effect on Photochromism and Photoconductivity

To check the aging effect (oxidation) on both photochromism and photoconductivity, the optical and resistivity measurements were repeated for SKY3 and SKY6 after 1 month. Fig. 15 shows the optical transmission from the repeated optical measurements on SKY3 and SKY6 after 1 month. We see that the photochromic response decreased significantly for SKY6 and almost disappeared for SKY3 (see Fig. 15) despite showing strong photoconductivity in Fig. 16. It was found that the photoconductive response almost did not change over time (comparing Fig. 13 (a, b) with Fig. 16 (a, b)). This shows that photochromism ceases quicker than photoconductivity.
Correlating Photochromism with Photoconductivity

In Fig. 17, the data from optical and the electrical measurements during bleaching are plotted in the same graph. The time dependence of the average transmittance (denoted by blue line) and resistance (represented by black and red line for illumination from front side and from substrate side, respectively) is shown for the samples during bleaching after 5 minutes of illumination (both normalized w.r.t the values before illumination). For all the samples, the photochromism is only few percent which is much less compared to photoconductive response. These plots show that the thinner samples show less photochromic response. SKY7 (the thinnest sample) did not show any bleaching rather it kept photodarkening (Fig. 17d in the bottom right panel). Probably, the probing light was too strong for the sample which might have initiated further photodarkening. In Fig. 17b, the high value of transmission after starting the illumination may be related to a time lag in data acquisition and exposure to the blue lamp. Moreover, as mentioned in section 6.2.2, again here, we can clearly see that during bleaching, the resistivity increases faster after front illumination compared to the back illumination (comparing black and red lines in each panel).
Another important thing we can see from above plots is that the resistivity curves for different samples during bleaching do not show any specific trend. There can be a qualitative connection between photodarkening/bleaching and conductivity, but they follow different time dependence, which indicates that the photochromic effect and the photoconductivity have, at least, partial different physical processes underlying them.

In Fig. 18, I plot the change of resistance before and after illumination normalized w.r.t the initial value vs photochromic response which is the change of intensity of the transmitted light before and after the illumination normalized w.r.t initial value. The plot shows a correlation between photoconductivity and photochromism. Stronger photochromic response corresponds to higher photoconductivity. We can also see that the repeated measurements on SKY3 and SKY6 after 1 month show that both the photoconductivity and photochromic response decreased for the samples over time. Sample age during
the measurements is presented in the table on the right. This aging is oxidation. Photochromic thin films oxidize with age and gradually lose photochromic response and photoconductivity.

![Photochromic thin films oxidation](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Age (days) during measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>optical</td>
</tr>
<tr>
<td>SKY3</td>
<td>29</td>
</tr>
<tr>
<td>SKY6</td>
<td>6</td>
</tr>
<tr>
<td>SKY8</td>
<td>4</td>
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<td>SKY7</td>
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<td>65</td>
</tr>
<tr>
<td>SKY6_repeated</td>
<td>42</td>
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</tbody>
</table>

*Fig. 18: Photoconductive response vs photochromic response. Samples were illuminated for 5 minutes.*

9 Final Observations

In this work, I grew a series of photochromic YHO quadruplet samples with variable thickness using reactive magnetron sputtering and performed compositional, optical as well as resistivity measurements on them. Following is the summary of observations from this project. During bleaching the resistivity increases faster after front illumination compared to the back illumination. The resistance during bleaching does not increase exponentially with time. In fact, the trend looks different for different samples under the same illumination time or same sample with different illumination time. Moreover, in this project, photoconductivity is observed irrespective of photochromism. Aged sample that almost lost photochromism due to oxidation, still showed strong photoconductivity. That means photochromism ceases quicker than the photoconductive behavior. Opaque samples also showed weak photoconductivity. Thus, we can conclude that photochromism and photoconductivity are not directly related. Furthermore, it was observed that photoconductivity is a bulk effect which increases with film thickness and saturates for thick films above 500 nm. Photoconductivity may be explained by the semiconductive nature of the material and the band gap. On the other hand, photochromism might rather be explained by the two-phase nature of the material with hydrogen moving from one phase to another as hypothesized in Ref. [12]. According to this hypothesis, a strong correlation between photochromism and transport properties is not expected which is in line with the finding of this project.
10 Future Directions for Research on Photoconductivity

The sample age during measurement is critical for correlating different properties of the photochromic samples. Samples could have shown better correlations if measurements were done simultaneously on samples of same age. The samples grown in this project showed maximum 8.6% of photochromic response after 5 minutes of illumination. The findings from experiment should be verified with samples with higher photochromic response. The experiment can also be repeated using different colors of illuminating lamps or using other REMHO thin films. In addition, the samples could be capped and checked if capping helps to delay the loss of photochromism. This should allow to quantitatively relate the photochromism to photoconductivity and reveal the different underlying physical processes.

References


Appendix

Fig. 19: Depth profiles of the samples a) SKY3, b) SKY6, c) SKY8, and d) SKY7 obtained from ToF-ERDA measurement data.
Fig. 20: RBS spectrum of the samples a) SKY3, b) SKY6, c) SKY8, and d) SKY7 with SIMNRA fit.