TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Materials and Environmental Technology

ENCAPSULATION OF YTTRIUM OXYHYDRIDE WITH THIN FILM OF AL_2O_3 OR TIO_2 GROWN BY ATOMIC LAYER DEPOSITION

ÜTRIUMOKSÜHÜDRIIDI KAPSELDAMINE AATOMKIHTSADESTUSE MEETODIL KASVATATUD ALUMIINIUMOKSIID VÕI TITAANOKSIID ÕHUKESTE KILEDEGA

MASTER THESIS

Üliõpilane:	Tero Lahtinen
Üliõpilaskood:	194197KAYM
Juhendaja:	Merike Kriisa

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(*On the reverse side of title page*)

AUTHOR’S DECLARATION

Hereby I declare, that I have written this thesis independently.
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Author:
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Department of Materials and Environmental Technology

THESIS TASK

Student: Tero Lahtinen, 194197KAYM

Study programme, KAYM, Materials and Processes of Sustainable Energetics

main speciality: Materials for sustainable energetics

Supervisor(s): Dr. Merike Kriisa +37 2620 3369, Dr. Smagul Karazhanov +47 965 17 797

Thesis topic:

(in English) *ENCAPSYLATION OF YTTRIUM OXYHYDRIDE WITH THIN FILM OF AL_2O_3 BY ATOMIC LAYER DEPOSITION*

(in Estonian) …………….……………………………………………………………………………….

Thesis main objectives:

1. To encapsulate YHO films by Depositing ~30-50 nm thick Al_2O_3 and TiO_2 by ALD with various deposition parameters
2. Study optical, structural and morphological properties of the films before and after they are illuminated by UV light
3. Perform annealing at different temperatures and study optical properties of the films before and after illumination with UV light.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Necessary data has been obtained	10.4.2021
2.	Thesis is sent to supervisors	30.4.2021
3.	Corrections to thesis have been done based on supervisors comments	17.5.2021

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Student: Tero Lahtinen 18.5.2021a

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Supervisor: Merike Kriisa ……………………….. “.......”......................20….a

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Consultant: ………………… ………...................... “.......”......................20….a

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Head of study programme: Sergei Bereznev “.......”......................20….a

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PREFACE

This study was supported by Project PRG627 “Antimony chalcogenide thin films for next-generation semi-transparent solar cells applicable in electricity producing windows‟ financed by Estonian Research Council, the Centre of Excellence Project TAR16016EK, financed by Estonian Research Council, Horizon 2020 ERA Chair Emerging next generation photovoltaics, 5GSOLAR (2020-2026) Grant agreement ID: 952509, financed by the European Commission, and ERDF project „Center of nanomaterials technologies and research (NAMUR+)” (2014-2020.4.01.16-0123).

The thesis has been done in cooperation with Institute of Energy Technology (IFE) of Norway and was mainly conducted in Tallinn University of Technology (TalTech). The team of supervisors of this thesis consisted of Dr. Merike Kriisa (TalTech), Dr. Smagul Zh. Karazhanov (IFE), Dr. Ilona Oja Acik (TalTech), and Dr. Elbruz Murat Baba IFE. In addition to supervisors, I would like to thank all the laboratory personnel at TalTech who helped me with my thesis and with learning how to operate the machinery: Atanas Katerski (Atomic layer deposition), Arvo Mere (X-ray diffractometry), Erki Kärber (Ultraviolet visible light spectroscopy) and Valdek Mikli whom I never met but who provided excellent scanning electron microscopy (SEM) images.

In the thesis encapsulation of potential smart window material, photochromic yttrium oxyhydride (YHO) was studied. The encapsulation was done with thin film of Al_2O_3 and TiO_2 deposited using ALD. Al_2O_3 thin film reduced YHOs reactivity with air but slowed down bleaching rate of YHO from dark state to transparent state. TiO_2 did not experience as strong loss in bleaching rate but experienced loss of photochromicity.

Keywords: Yttrium oxyhydride, photochromic, atomic layer deposition, encapsulation, master’s thesis

List of abbreviations and symbols

ALD = Atomic layer deposition
Al_2O_3 = Aluminium oxide
GPC = Growth per cycle
IEA = International Energy Agency
IFE = Institute of Energy Technology
SEM = Scanning electron microscopy
TiO_2 = Titanium oxide
TMA = Trimethyl aluminium
UV = Ultraviolet
UV-Vis = Ultraviolet visible light spectroscopy
XRD = X-ray diffractometry
YH_2 = Yttrium hydride
YH_3 = Yttrium trihydride
YHO = Yttrium oxyhydride

INTRODUCTION

Today nearly 20% of the total electricity used in buildings is consumed by cooling systems according to International Energy Agency (IEA) report *The future of cooling*. From 1990 to 2016 the use of energy for indoor space cooling has more than tripled and the demand is growing especially due to economic and population growth in the hottest parts of the world. According to the IEA report, one of the ways to reduce the need for indoor space cooling is solar protection of the building, e.g., by using better windows that do not let heat in as much as traditional ones. [1]

Smart windows can prevent solar radiation from entering the building by changing from transparent to dark. Colour changing smart windows can be divided in passive and active control windows. Passive control windows do not need to be activated by an operator, but they react to a natural stimuli for example light (photochromic materials). In a review on passive and active smart window technology in 2014 smart windows on the market could go, for example, from 65% transparent to as low as 0.5% or alternatively from 75% transparent to 50% at dark state. [2]

One of the inorganic photochromic materials that poses a possibility to function as smart window material is yttrium oxyhydride (YHO). YHO was discovered approximately 10 years ago by Trygve Mongstrad in Norway and unlike YHOs predecessor photochromic yttrium hydride systems, YHO is reversibly photochromic in atmospheric conditions. [3] The transparency of YHO film can be typically reduced from 80-90% in clear state to 30-40% in dark state in visible light region. Even though YHO is fairly stable in atmospheric conditions it has been reported to oxidise in temperatures above 100°C [3] and slowly hydrolyse in liquid water. [4] One way to prevent reactions between YHO and its environment is encapsulating it with material that prevents YHO from reacting with atmosphere.

In this study YHO was encapsulated with Al_2O_3 and TiO_2 deposited by atomic layer deposition (ALD) and YHOs photochromic performance before and after annealing in 100-150°C was studied. Al_2O_3 encapsulated samples showed improved resistance to annealing, one of the samples studied had change in contrast of 18 % points in total transmittance ("transparency") after 30 min ultraviolet (UV) light exposure and decrease of up to 47 % points in total transmittance after 16h UV exposure. However improved resistance to environment came with a price of longer bleaching time. TiO_2 encapsulated samples' photochromic performance deteriorated but their bleaching rate was better than Al_2O_3 encapsulated and annealed reference sample.

1 Overview on literature

Yttrium oxyhydride is a reversibly photochromic material that could be used in smart windows that automatically blocks sunlight from entering a building. YHO may however be unstable in atmosphere. [3, 4, 5] To prevent reactions with atmosphere YHO can be encapsulated with a thin film of another chemical.

Thin films are a commonly used method to encapsulate materials that may react with atmosphere and atomic layer deposition (ALD) is one of the state-of-the-art equipment's to deposit ultrathin films in low temperatures. Few examples of the chemicals that can be deposited using ALD are TiO_2 and Al_2O3. [6, 7]

In addition to YHO being mildly unstable in atmosphere at room temperature, it oxidizes strongly at temperatures above 100°C. Oxidation can be used to tune the colour and photochromic properties of YHO samples [3] and to accelerate transition of the samples from dark to transparent state [8]. In addition, if encapsulated YHO sample would oxidise less than a sample that has not been encapsulated, it could be concluded that encapsulation provides additional protection against change in the sample, which is what has been done in this research.

To confirm that changes have not/have taken place in a YHO sample during annealing in above 100°C temperature, X-ray diffractometry (XRD) can be used to study changes in the crystal structure [9] and, ultraviolet visible light spectroscopy (UV-Vis) can be used to study the optical properties. [10] One of the best tools to confirm successful growth of Al_2O_3 and TiO_2 is scanning electron microscope (SEM) that takes images of the samples with nanometre accuracy. [11]

1.1 Short introduction to smart windows

Smart windows that prevent solar radiation from entering a building by changing their colour from transparent to dark can be divided in two categories: passive and active control. Passive smart windows do not require external power, presence of human, and active interaction for their operation but respond to natural stimuli such as light (photochromic materials) or heat (thermochromic materials). The strength of a passive system over an active system is simple design, low cost, easy installation and reliability, and the strength of an active system is that it can be controlled by user or automatic building management system. However, design of the active system is complicated, they are high cost >300 USD/m2, and there are some drawbacks upon applications in realistic conditions such as non-uniformity of colour change, degradation of the device, etc. In a review on different smart glass technologies done in 2014 smart windows contrast that changed from 65 % total transparency to as low as 0.5 % or alternatively from as high as 75 % transparent to 50 %. [2]

Photochromic glass or glazing is a passive control system in which transparency of glass changes in relation to incident light intensity due to organic or inorganic compounds that, for example, react with ultraviolet part of sunlight. The speed of response is of the order of few minutes and generally transformation from tinted to transparent state is twice as long. Current challenges of photochromic materials are gradual loss of the reversibility of the process over time, difficulty to achieve uniform distribution of photochromic substance and high cost. Despite of the challenges photochromic glass is already used in optical industry and car industry. [2]

1.2 Yttrium oxyhydride

Yttrium oxyhydride is a mixed-anion compound that possesses reversible photochromic properties that can be tuned by oxidising the samples in elevated temperature. [5] The events that take place inside YHO during photodarkening are still not clear but some theories do exist and have been tested: gradual growth of dark metallic domains [12], reversible diffusion of hydrogen [8] and oxygen exchange in the crystal structure of YHO. [10]

Advantage of the yttrium oxyhydride over other photochromic films is that upon colour change, transmittance almost evenly charges on all photon wavelength region from fundamental absorption edge to far infrared light. These exciting materials properties present interest for practical applications in windows. One of the challenges limiting commercialization of the product in the market is suppression of oxidation of YHO and light-induced O/H release from the films that might lead to degradation of the film. One of the ways of mitigation of the challenge is encapsulation with a wide band gap material. [13]

1.2.1 **Oxyhydrides**

Oxyhydrides are part of mixed-anion compounds group. Mixed-anion compounds are solid-state materials containing more than one anionic specie in a single phase. The anionic characteristics, such as charge, ionic radii, electronegativity, and polarizability bring new possibilities to control and adjust material properties which might not be possible for single-anion material. Some of the many functions achieved with mixed-anion compounds are superconductivity, energy storing, thermoelectricity [14] and photochromism. [15]

Oxyhydrides are a rare form of material that contain oxide and negatively charged hydride (H-) anions. In 2018 there were 1266 oxyfluorides but only 47 oxyhydrides in Inorganic Crystal Structure Database. The number can be further compared to number of oxides in the data base which was between 45 000 – 55 000.

Some of the fascinating properties of hydride anions are:

- flexibility in size, with the ionic radii of 130-153 pm
- bipolarity and moderate electronegativity allow covalent, metallic, and ionic bonding (b)
- lack of π symmetry allows H- to function as "π-blocker" or "orbital scissors" between t2g orbitals of transition metal. (c)
- mobile around their central ion. (Figure 1)

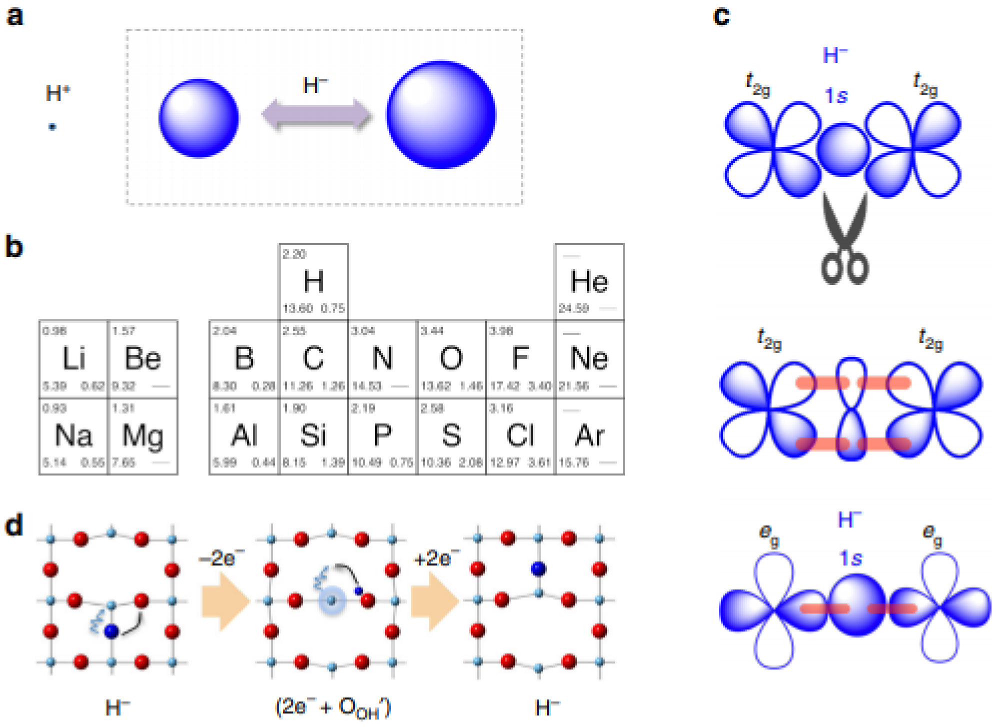


Figure 1 Features of hydride ion. A) size flexibility b) periodic table based on electro negativity (upper left), ionization potential (lower left), electron affinity (lower right) d) hydride anion conductivity and c) lack of π symmetry allows hydride ion to function as a "π-blocker" also σ bonding between is suggested between e_g and H– 1s orbitals. [14]

Understanding of these properties of hydride ion is not essential later in this paper but they describe well the complexity of possible reactions and events that can take place in oxyhydrides.

1.2.2 **Discovery of yttrium oxyhydride**

Yttrium oxyhydride is a photochromic material that is relatively stable under atmospheric conditions. It was discovered by Trygve Mongstrad in Kjeller Norway in the Institute for Energy Technology and the findings were first published in 2011. Before this discovery yttrium-hydrogen systems had been studied for over 15 years due to yttrium metals change into yellowish transparent semiconductor yttrium trihydride after hydrogen uptake. [16, 17] Before discovery of YHO, photochromism of yttrium hydrogen system was only reported at extremely low temperature [18] and in hydrogen pressurized to 5.8GPa with high light intensity [19].

First, YHO thin films were prepared with reactive magnetron sputtering and oxygen was incorporated unintentionally into the crystal structure. The presence of water vapour in the reaction chamber was at first expected to be the reason for oxygen in the lattice. The oxygen was discovered with Rutherford back scattering spectrometry and neutron reflectometry measurements which gave an estimated 8-32 at% of oxygen in the deposited thin films. The distribution of oxygen on the film is isotropic excluding oxidised surface layer that protects the rest of film from oxidation and hydrogen desorption. [20] Later on it was noticed that oxidation does not necessarily take place in the reaction chamber and the sputtered samples are actually YH_X (believed to be YH_2) films which upon reaction with air expand and turn into YHO. [21]

1.2.3 **Tailoring the colour of YHO sample before UV exposure**

The relation between photochromic properties of YHO and ratio of hydrogen, oxygen, and yttrium was studied in 2017 by making a sample with lateral gradient (76x26 mm^2) by sputtering a glass substrate while keeping the substate in fixed position during deposition. (Figure 2) [22]

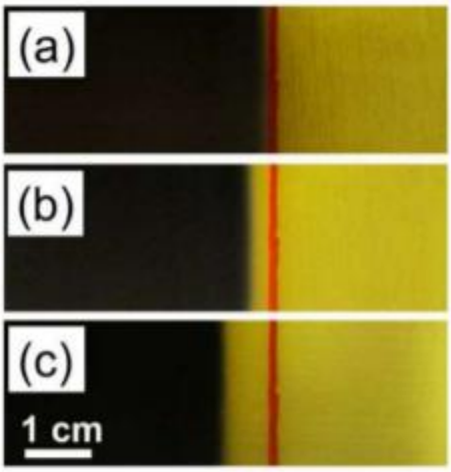


Figure 2 Photographs of the samples after a) 2h b) 24h c) 57 days after deposition in air exposure. [22]

After 21 days from deposition the samples were measured using time-of-flight energy elastic recoil detection analysis to learn the ratio of hydrogen, oxygen, and yttrium at different points of the samples. (Figure 3) [22]

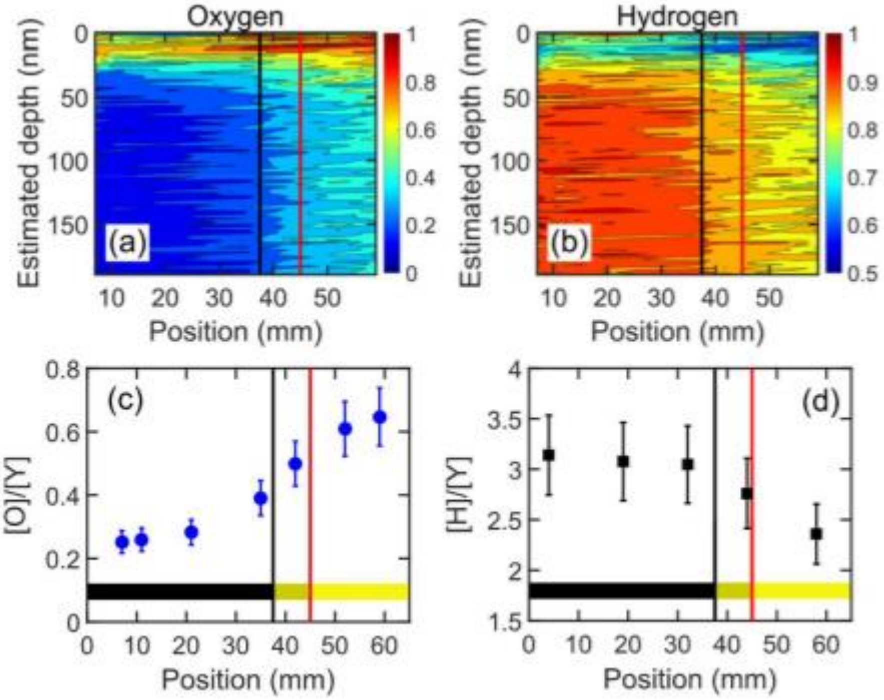


Figure 3 Normalized and interpolated maps of a) oxygen and b) hydrogen. Average bulk c) O/Y and d) H/Y ratios plotted at different points of the 76mm long substrate. Red line indicates the boundary position of black and yellow part after deposition and black line at time of measurement. [22]

In figure 3 its shown that the film starts to turn transparent approximately with O/Y ratio of 0.45. Also, the earlier mentioned thin oxide layer on the top of the samples can be seen in the figure. It was also discovered in the same study that within the transparent area of the film the band gap increases (from 2.83-2.93eV) with increasing oxygen concentration and at the same time photochromic response reduces due to reduced light absorption. [22]

1.2.4 **Photochromicity of YHO**

Absolute certainty of the photochromic mechanisms in YHO are still uncertain but theories and studies to support the theories have developed during the years. Phenomena that cause and impact the reversible photochromic behaviour of YHO are: lowering of band gap with lower oxygen concentration [5], lattice contraction and activation of charge carriers [23], formation of metallic domains [12], hydrogen mobility in lattice [24], structural changes and oxygen diffusion and exchange with environment [10].

Already in the first publication of Trygve Monstrad et al on YHO it was discovered that oxygen was a crucial element for photochromism to occur in room temperature but intriguingly the samples with lowest oxygen content had the strongest photochromic response to light. It was also noticed that the sputtered YHO samples had YH_2 like fcc lattice while transparent YH_3 has hcp crystal lattice. Also, increase in band gap was noticed as the oxygen content increased and it was suggested that this could be partially or wholly the reason for photochromic behaviour. [5]

Lattice contractions and charge carriers. In 2013 YHO samples were studied in time-resolved synchrotron radiation-based X-ray diffraction. Three samples were studied of which two were transparent and one black. The first finding was that the photo darkening was also triggered by x-rays suggesting that excited charge carriers can also provoke photodarkening. The experiments also showed that blue light and UV-light trigger the reaction stronger than other wavelengths. It was also noticed that lattice contractions took place for all the samples including the dark one suggesting that reconstructing happens in more general level not only when photochromism takes place. A hypothesis was drawn that photon absorption triggers H and/or O shifting from their location, which in turn contracts the lattice. [23]

Formation of metallic domains. Study published on 2017 successfully reproduced the optical properties of YHO film before and during illumination using the effective medium model. This suggested that photodarkening can be explained quantitatively with Maxwell-Garnett approximation, by gradual formation of small metallic domains in semiconducting lattice upon illumination that cause the decrease in transmittance of light. However, it remained unclear what is the role of oxygen in this process and why is the darkening reversible. [12]

Hydrogen mobility. In 2014 Chandran C.V. et al found three hydrogen species with different mobilities in nuclear magnetic resonance spectrum of YHO samples. Upon illumination the most mobile hydrogen species disappeared. In 2019 study of Zhang Q. et al also concluded that H migration plays a role in photochromicity of YHO. In the study YHx:O/WO_3 composite film was studied with Fourier transform infrared spectroscopy. For transparent samples special absorption of YH_3 was found but it disappeared after illumination. [24]

Structural changes and "breathing". Publication in 2019 showed that the photodarkening can be triggered without significant composition changes taking place in high vacuum environment, meaning that reactions with atmosphere are not necessary. This finding suggests that photochromism is caused by structural changes and/or electronic rearrangements. [15] Even though photodarkening can be triggered in vacuum bleaching rate is greatly impacted by the environment as can be seen in figure 4 taken from study of Baba. E.M. et al where bleaching of YHO samples was studied in air and in glovebox with N_2 atmosphere. [10]

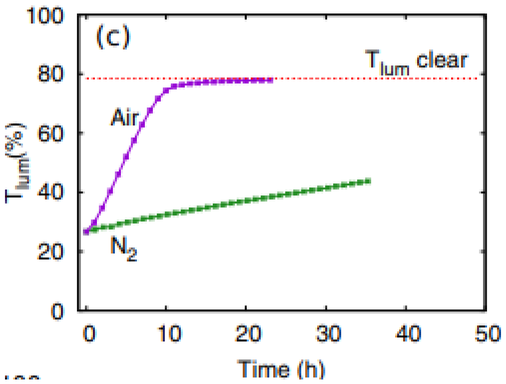


Figure 4 Difference in recovery of YHO samples bleached in air and in N_2 by measurement of luminous transmittance. [10]

The study of Baba E.M. et al concluded their findings on photochromicity of YHO with following words: "*When exposed to air the YH_2 lattice expands from 5.20 to 5.34 Å due to the incorporation of oxygen. In addition to the lattice expansion, YH_2 turns into YHO. YHO is transparent and photochromic. The reversibility of the photochromic* *effect depends on the surroundings of the films, being a source of oxygen necessary for the adequate bleaching of the samples. Therefore, the photochromic mechanism must involve oxygen diffusion and oxygen exchange between the sample and its surroundings. A consequence of the oxygen diffusion is the unusual enhancement of the hydrophobicity and the reversible lattice contraction of the YHO films under illumination.*" [10]

1.2.5 **Crystal structure and optical properties of YHO**

Yttrium oxyhydride shares some differences and similarities with compounds of yttrium and hydrogen. From optical point of view YHO can be yellow transparent like γ-phase yttrium trihydride (YH_3) and it can be dark like metallic β-phase yttrium dihydride (YH_2) but despite of the colour the crystal structure of YHO is FCC like YH_2 and unlike YH_3 which has HCP structure. [5]

Crystal orientation of transparent and dark YHO samples is different as can be seen in figure 5. For transparent samples crystal orientation (200) dominates over black one and vice versa for crystal orientation (111). It can be also noticed from the figure 5 that YHO shares little similarities with Y_2O_3. [5]

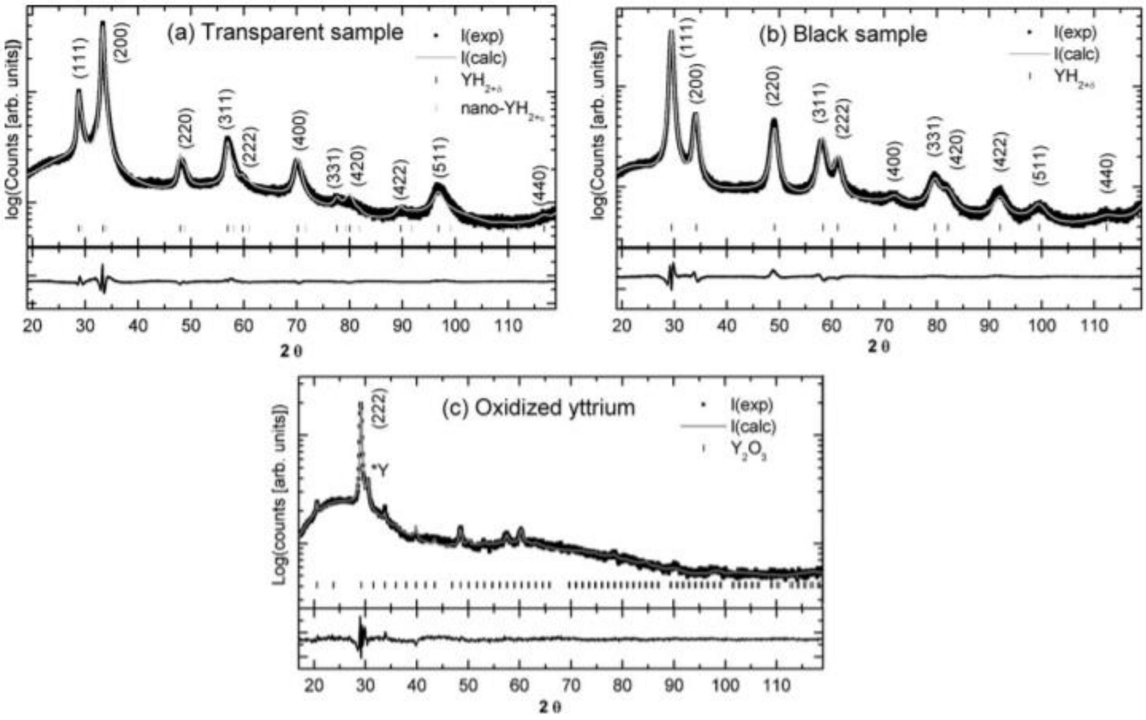


Figure 5 XRD results of (a) transparent and (b) black YHO films in comparison with (c) transparent Y_2O_3 film. [5]

When it comes to producing dark or transparent YHO, deposition pressure of hydrogen in magnetron sputtering plays a key role. In figure 6 it can be seen that dominating (200) has been achieved at 1 Pa pressure whereas depositions at 3 and 6 Pa have resulted in dominating (111) peak. [9]

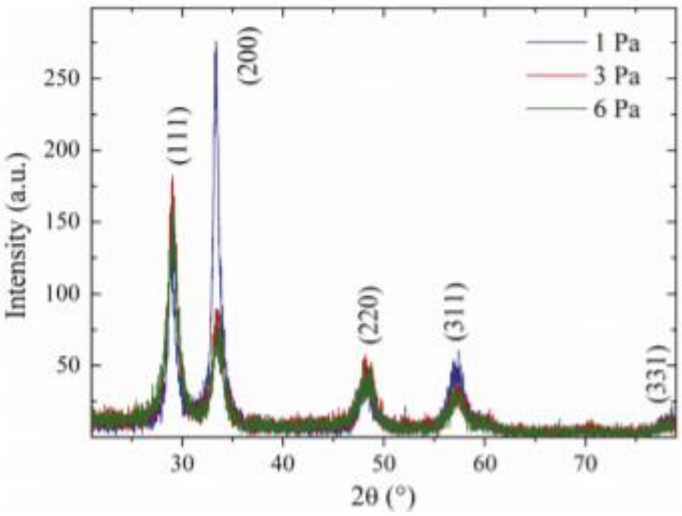


Figure 6 Relation between deposition pressure and crystal orientation. [9]

In a study of You et al. it was discovered that greater deposition pressure gives YHO more Y_2O_3 like band gap (5.5 eV) and lower deposition pressures result in band gap similar to YH_3 (2.6 eV). [25]

1.2.6 **Behaviour in elevated temperatures**

In study by Dmitrii Moldarev et al several YHO samples were annealed in atmosphere in different temperatures for 30 minutes and after this their compositions were deducted from time-of-flight elastic recoil detection analysis. As it can be seen in Figure 7 temperatures of over 100°C (373 K) lead to strong oxidation of the samples and increasing oxygen concentrations leads to decrease in photochromic response. [3]

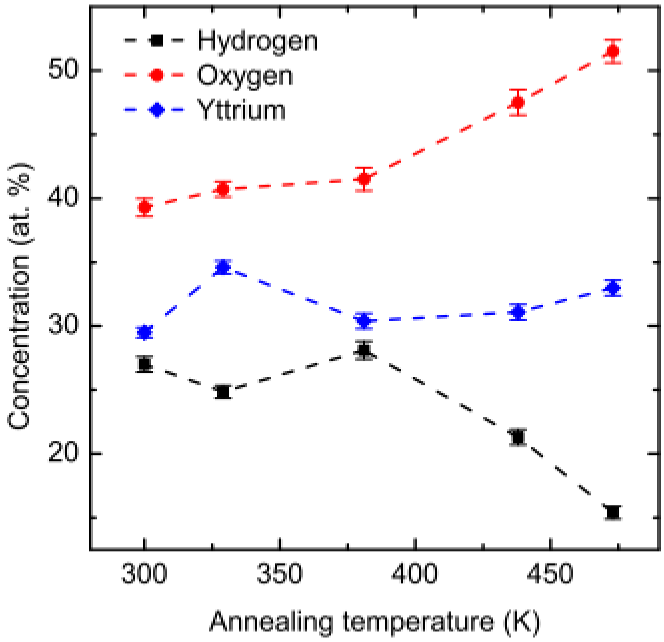


Figure 7 Composition of samples after annealing for 30min in different temperatures [3]

The annealing also led to higher total transmittance of the samples which means that annealing can be also used for tailoring the colour of the samples after deposition. [3]

In XRD patterns, oxidation of samples can be especially seen in leftwards peak shift and change in intensity of peaks (111) and (200). In figure 8 grazing-incidence x-ray diffraction patterns of YHO sample with gradual gradient can be seen. [26]

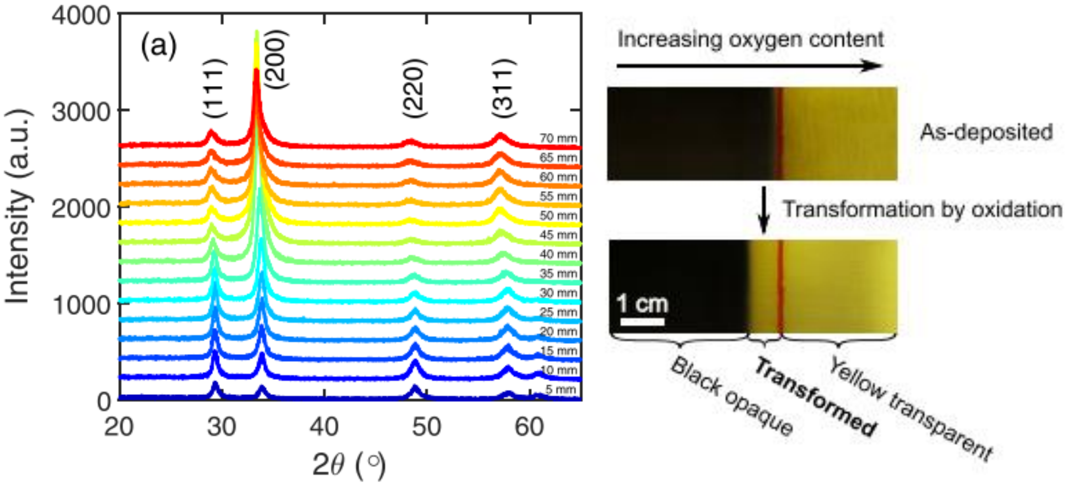


Figure 8 On left XRD patterns of a sample 90 days after deposition. On right below the sample 57 days after deposition. "5 mm" XRD pattern corresponds to far left of the

sample, “70 mm“ to far right and red line on the samples is located between “40-45mm“. [26]

Peak corresponding to (200) crystal orientation has the highest intensity at 40mm. In the same study it was found that at 40mm the sample had lowest amount of oxygen in comparison with 45-65 mm. At 40mm the photochromic response was the strongest, but the bleaching time was the slowest. [26]

1.3 Encapsulation with atomic layer deposition

In encapsulation an active compound “the core” is stabilized with a structure “the shell” that does not negatively impact the chemical, physical or biological properties of the material. [6] Atomic layer deposition (ALD) is a technique that enables encapsulation of a material with an ultrathin film (tens of nanometres) and is widely used, for example in encapsulation of organic light emitting diodes to prevent oxygen and moisture damage. [27]

Atomic layer deposition (ALD) is a gas/vapor state chemical thin film deposition method and few of its key advantages are ability to cover complex 3D shapes, high purity of the product [28] and ability to do depositions at low temperature [7]. The high quality of deposition comes with a price of a lot of time spent for deposition. [28]

The growth of thin film in ALD builds up in cycles and a typical cycle consists of four steps:

1. Precursor pulse. Precursor is typically inorganic metal centred compound with functional groups attached to it.

2. Purging of reaction products.

3. Co-reactant pulse. Typically involving a small molecule.

4. Purging of reaction products. (Figure 9)

The reactions that take place during precursor pulse and co-reactant pulse are self-limiting meaning that the process stops when all reaction surfaces are occupied. The films grown in ALD are generally amorphous but in some cases polycrystalline. [7]

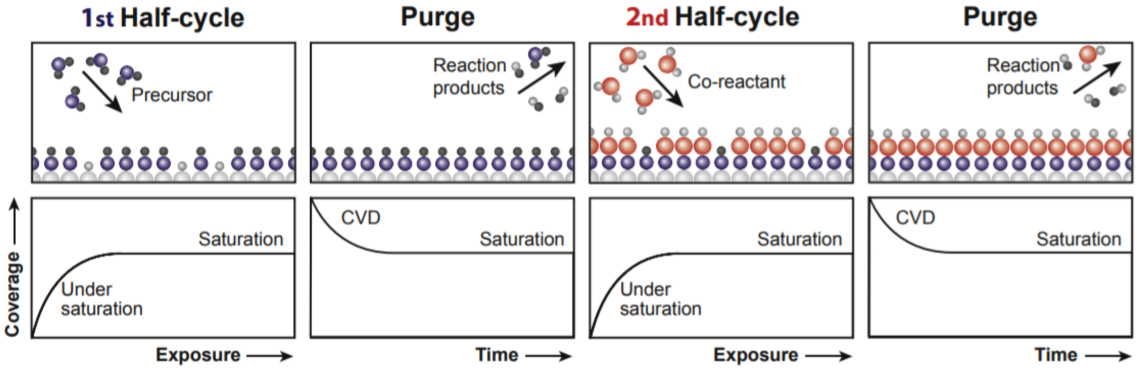


Figure 9 A schematic representation of an ALD cycle in upper panel. The lower panel shows the achieved coverage per cycle. If exposure time of reactants is too low or if purging time is too low the ideal growth is not achieved. [7]

Conditions to achieve self-limiting growth and high-quality film differ for every precursor and co-reactant used. The ideal temperature for film growth is called temperature window. In figure 10 the temperature window can be seen as horizontal line and on left and right side of the line possible consequences of operating ALD outside of temperature window is shown. [7]

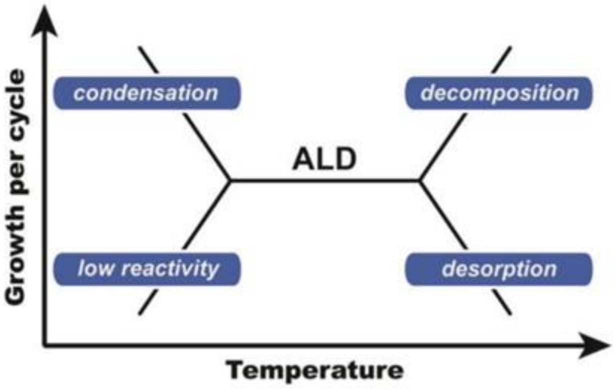


Figure 10 The ideal temperature window in ALD. Whether too low temperature results in condensation and high growth per cycle (GPC) or low reactivity and low GPC depends on precursor and co-reactant. Also, what happens in temperatures above the ideal state depends on chemicals used. [7]

Operating outside the temperature window does not necessarily mean that deposition will fail however it can come with the cost of low material purity, low growth per cycle (GPC), or long cycle times.

In addition to temperature the substrate plays a role in the early stages of thin film growth by delaying or accelerating the growth (Figure 11). For example, delayed growth occurs if the initial surface has limited number of groups that react with chemicals used in ALD. In delayed growth the growth starts with formation of isolated islands and only once the islands have grown enough to meet each other the stable growth starts. [7]

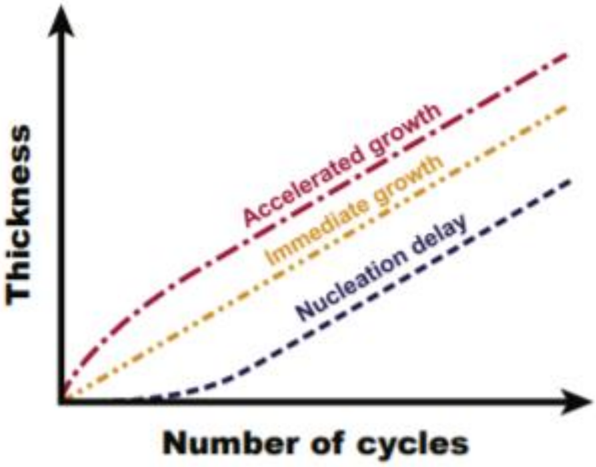


Figure 11 Different nucleation behaviour of ALD film: accelerated growth, immediate growth (ideal) and nucleation delay. [7]

1.3.1 Al_2O_3 deposited with ALD using Triethylaluminium and water

Al_2O_3 can be deposited in ALD using various co-reactants and aluminium attached to different functional groups. In a deposition where trimethylaluminium (TMA) and water are used the two half reactions happen in following way:

$$\mathrm{s - OH(ads) + \tfrac{1}{2}\,[Al(CH3)3]2\ (vap) \rightarrow s - OnAl(CH3)3 + n\,CH4(g)}$$

The ideal temperature window of Al_2O_3 deposition using TMA is typically around 200-300°C where it reaches GPC of 1 Å/cycle. By multiplication of pulsing cycles high thickness per cycle can be achieve even in low temperatures as can be seen in figure 12, however if pulsing cycles are multiplied deposition time is multiplied as well. [29]

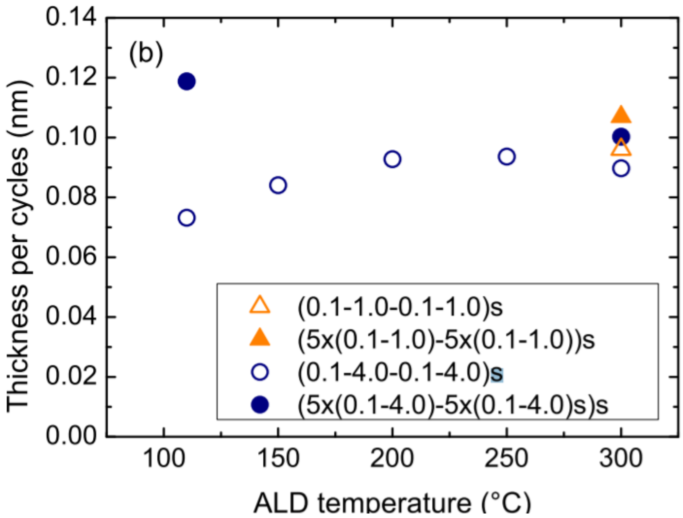


Figure 12 Relation between temperature and growth per cycle. [29]

In addition to lowered GPC the impurity concentration rises as the process temperature goes down. The impurities come from methyl groups that have not been replaced by OH groups during second half reaction. (Figure 13)

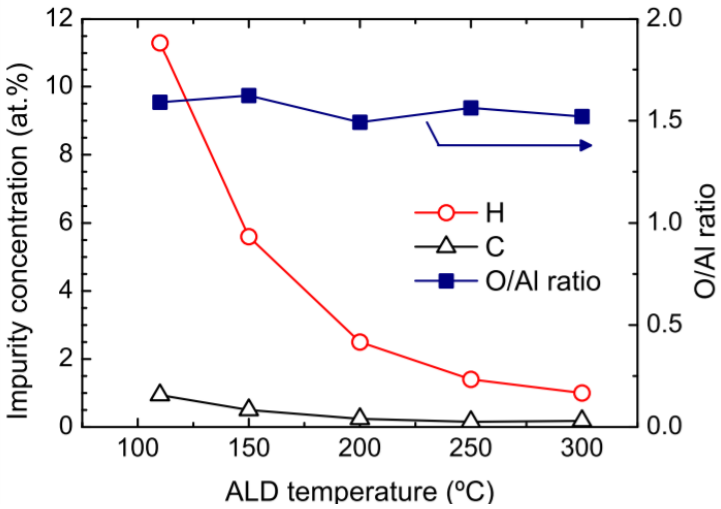


Figure 13 Realition between deposition temperature and aluminum and per oxygen ratio amd content of hydrogen and carbon impurities [29]

Other unwanted impacts that can occur in deposition at low temperature are [29]:

- Lower hardness
- Lower elastic modulus
- Lower density
- Higher residual stress

In a study on structural and optical properties of Al_2O_3 deposited by ALD impact of number of cycles on optical properties of Al_2O_3 thin film were studied. The deposition was done using TMA in 200°C temperature with silicon substrate. In the study it was found that absorption coefficient (the higher the absorption coefficient the shorter wavelengths of light can penetrate into a material [30]) starts to increase from zero after 3 eV (from approximately 400nm to lower wavelengths) and the thicker the film the faster the absorption coefficient increases, as it can be seen in figure 14. [31]

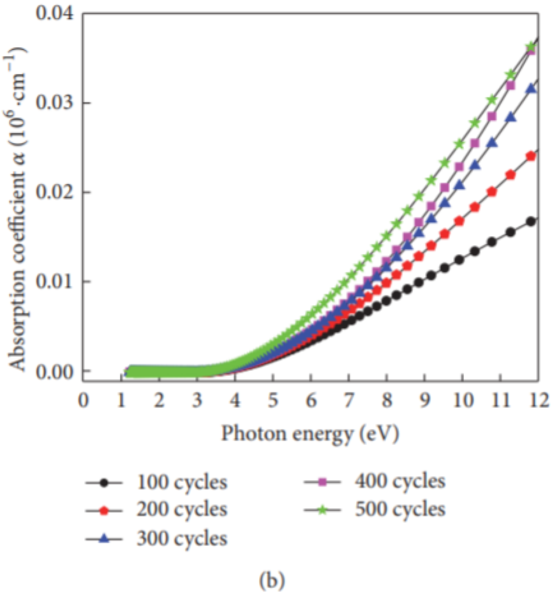


Figure 14 Impact of amount of cycles on absorption coefficient. [31]

In the same study the refractive index of Al_2O_3 was found to be approximately 1.5 for 100 cycles 1.6 for 200 cycles and around 1.7 for samples with 300-500 cycles. [31]

1.3.2 TiO_2 deposition with ALD

Like Al_2O_3 films also TiO_2 film can be grown using several different chemicals, one of them being the technique using titanium tetrachloride and water. The reaction is much like the reaction of TMA and H_2O except that the precursor is titanium with chloride as functional groups. The maximum growth per cycle for TiO_2 is achieved in 225-300°C but the behaviour at lower temperature is not as straight forward as the one of Al_2O_3. This can be seen from comparison of GPC versus temperature in figure 15. [32]

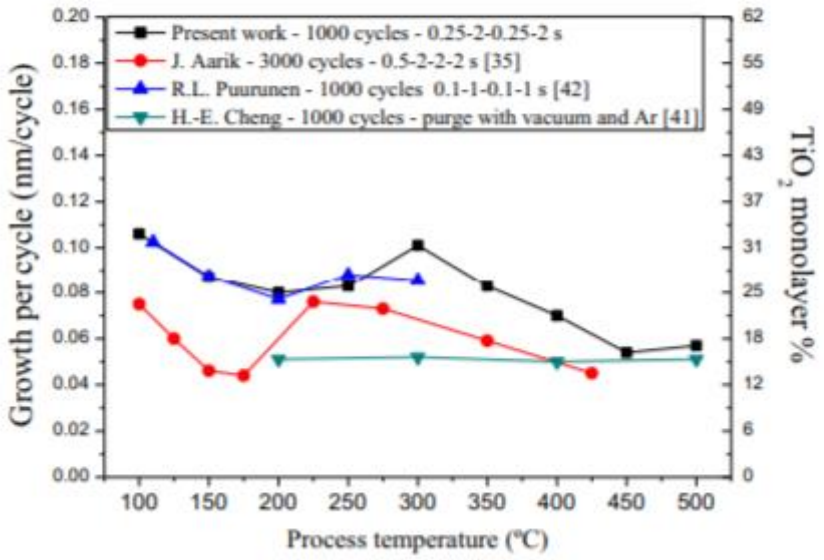


Figure 15 Impact of process temperature on GPC of TiO_2 [32]

The reason why GPC relation to temperature is so different compared to Al_2O_3 growth in ALD is due to formation of different crystal structures of TiO_2 at different temperatures. Grazing incidence x-ray diffraction and Raman analyses in the study of W. Chiappim et al showed that films deposited on FTO glass at temperature of 150-200˚C are amorphous, 250-300˚C anatase and above 300˚C rutile. [32]

O/Ti ratio has been reported to suffer as well as purity of the deposition as process temperature decreases. When operating below the ideal temperature window O/Ti stoichiometry deviates from ideal 2.0 ratio and chlorine concentration increases as can be seen in figure 16. [32]

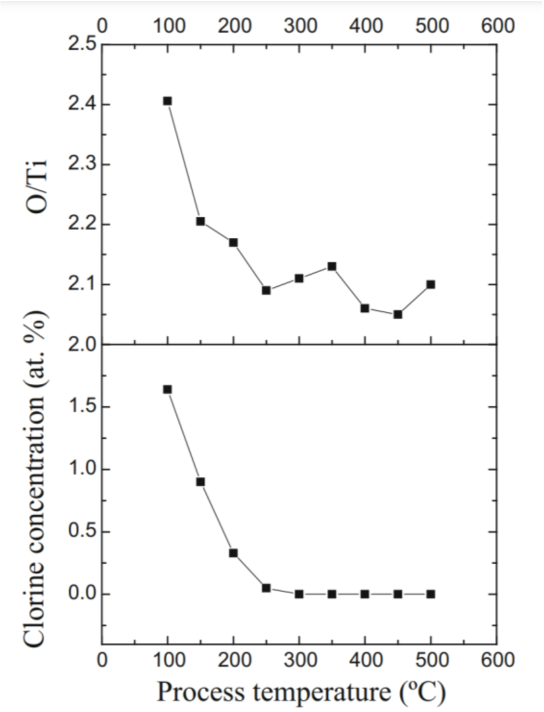


Figure 16 Impact of process temperature on TiO_2 stoichiometry. [32]

Unlike Al_2O_3 TiO_2 has absorption coefficient values of 0.1-0.2 μm^{-1} at wavelengths above 400nm. The absorption coefficient of TiO_2 starts to increase at lower wavelengths for films deposited in lower temperatures as can be seem in figure 17. [32]

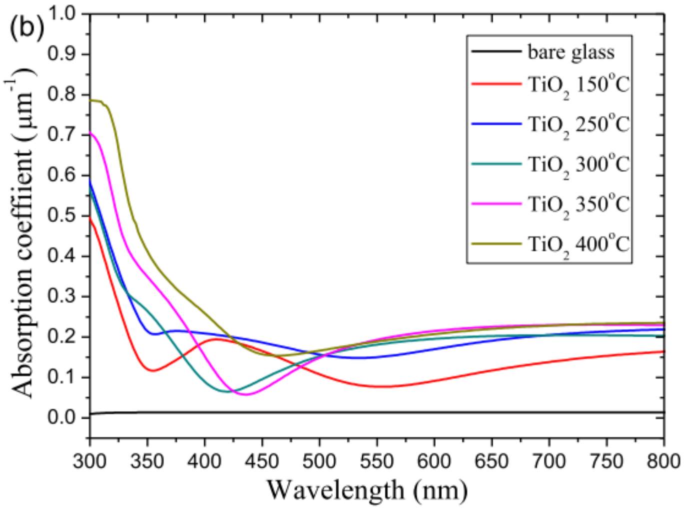


Figure 17 Impact of ALD process temperature on absorption coefficient of TiO_2 [32]

Optical band gap of TiO_2 grown in ALD at 100˚C has been reported to be 3.3 eV with refractive index of 2.2-2.3 at a wavelength of 633 nm. [33]

1.3.3 Possible interactions between YHO and Al_2O_3 or TiO_2 under annealing and UV-light exposure

For successful encapsulation TiO_2 or Al_2O_3 should not negatively alter chemical or physical properties of YHO during / after deposition, the properties should not change during UV-light exposure and the properties should remain unchanged after annealing in temperature of 100-150°C or at least should change less in comparison with non-encapsulated samples.

According to Chia Hsun Hsu et al ALD deposited amorphous TiO_2 film need to be annealed in temperature of 450°C before phase transition to anatase takes place. [34] TiO_2s phases rutile and anatase have band gaps of 3.0 and 3.2 eV (equivalent to energy of UV light) and can function as n-type semiconductors and form hydroxyl radicals in reaction with water in atmosphere and sunlight. These properties have made TiO_2 into promising photocatalyst for hydrogen production and air pollutant removal. [35] Mechanism of excitation and hydroxyl radical formation is demonstrated in figure 18.

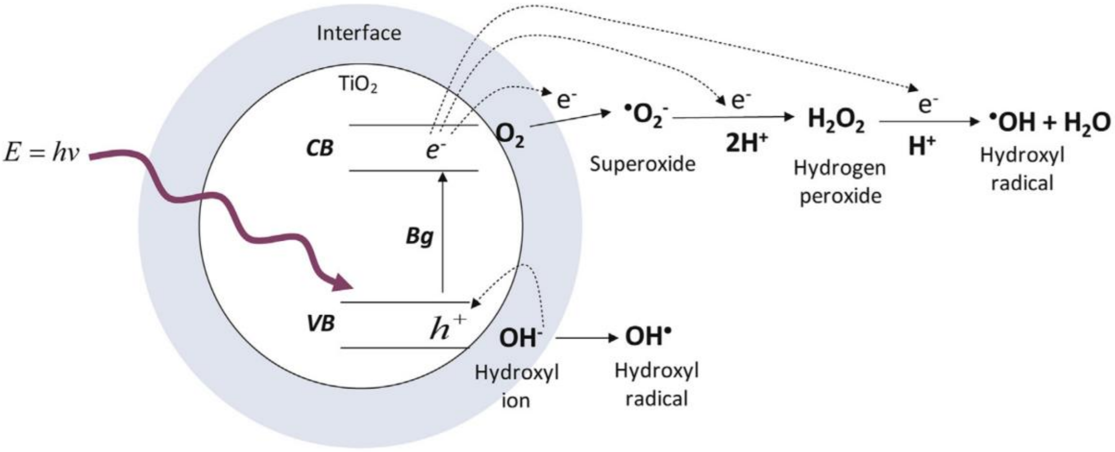


Figure 18 Photocatalytic reaction of TiO_2 with UV light. [36]

It has been reported by Kaur K. Et al that based on analysis of electric properties of amorphous TiO_2 it should work as photocatalyst even though not as efficiently as rutile and anatase. [37] If the reactions shown on in figure 18 take place with the hydrides and oxides of YHO it may result in unwanted changes in properties YHO.

Al_2O_3 is not generally activated by UV-light like TiO_2 due to much larger band gap of ~7 eV. [38] Also reactions with yttrium [39] and hydrogen take place in high temperatures. [40]

1.3.4 ALD in mass production

Based on brief review on ALD devices in the market now it can be concluded that when it comes to simple shapes, such as wafers, and very thin depositions it is possible to deposit as much as 4500 wafers per hour. [41] It is also possible to deposit substrates as large as 730 x 1200 mm with total batch size of up to 40 m^2 but it would seem that currently there is no ALD solution that would enable depositing large surfaces such as windows with fast pace. [42]

1.4 Summary of overview on literature and formulation of the thesis task

YHO is a material that shows great promise for passive smart windows applications due to its reversible photochromic behaviour. YHO is relatively resistant to atmospheric conditions but this might not be enough since smart window should have a lifetime of several, preferably tens of years. One approach to improve YHO performance in atmosphere is encapsulation and one of the state-of-the-art equipment for encapsulation is ALD. It might take years before ALD is ready for depositing full sized smart windows especially in industrial scale but now ALDs ability to deposit thin films in low temperature makes it a suitable device to study encapsulation of YHO which oxidizes in temperatures of above 100°C. Al_2O_3 is a promising encapsulant due to its large band gap which makes it less reactive under sunlight. However, there is a risk that blocking the interaction between air and YHO will make the bleaching very slow. TiO_2 has lower band gap making it potentially reactive with YHO especially under sunlight but it is also possible that these reactions have positive impact on the bleaching of the film.

Success of encapsulation can be studied among other laboratory instruments with XRD, UV-Vis and SEM. When exposed to elevated temperatures YHO becomes more transparent due to oxidation and its photochromic response to sunlight lowers as well, this changes in YHO can be recorded by using UV-Vis. The UV-Vis results however do not show if changes have happened in crystal structure of YHO. Changes in crystal structure can be studied using XRD. In XRD, peak shift of peaks (111) and (200) towards left suggests oxidation with an exception of right wards peak shift when YHO has oxidizes so far that it starts become Y_2O_3. Peak shift towards right takes place when YHO is exposed to light. Intensity of these peaks is the highest when oxygen content is very low and decreases if either oxygen or hydrogen content is increased. Scanning electron microscope (SEM) makes it possible to observe visually the quality of encapsulated YHO films.

The overall study was divided into three experiments that aimed to answer three different questions: 1. Can the encapsulation be done? 2. How ALD deposition parameters impact on YHO and encapsulation? 3. How sample preparation of YHO impacts encapsulation and properties of YHO?

2 Methods

In most of the experiments that were done there were several encapsulated samples and a few unencapsulated samples for reference. Samples were exposed to UV-light and elevated temperatures and the equipment used to study the samples were UV-Vis, XRD, SEM and cyclic testing device in IFE Norway.

In the first experiment a single YHO sample was encapsulated in moderate temperature. After successful first experiment second experiment focused on testing impact of deposition temperature and cycle amount on encapsulation and performance of YHO. In the third experiment YHO samples prepared with different deposition pressures in IFE Norway were encapsulated with ALD using temperature and cycles that gave the best results in the second experiment. A set of samples were also deposited in ALD using TiO_2 since this new precursor was bought to the laboratory and Al_2O_3 deposited samples suffered from long bleaching time.

2.1 Instruments and their purpose

Samples were encapsulated using Picosun R200 Atomic layer deposition device. Samples were exposed to UV using Philips TL-D 15W Actinic BL UV-A radiation lamp and annealed using Präzitherm hot plate. Samples were studied using Jasco, V670 optical spectrometer, Rigaku smart lab X-ray diffractometer and SEM imaging was ordered from SEM operator of TalTech.

2.1.1 **Picosun R200 atomic layer deposition device**

When depositing thin films with ALD different numbers of cycles (200-400) and temperatures (100-200 °C) were used. The parameters used in each deposition are told in detail in the measurement sections. The precursors used were trimethyl aluminium, TMA ($Al(CH)_3$) and titanium tetrachloride ($TiCl_4$) and co-reactant was water (H_2O). The ALD set up can be seen in picture 1.

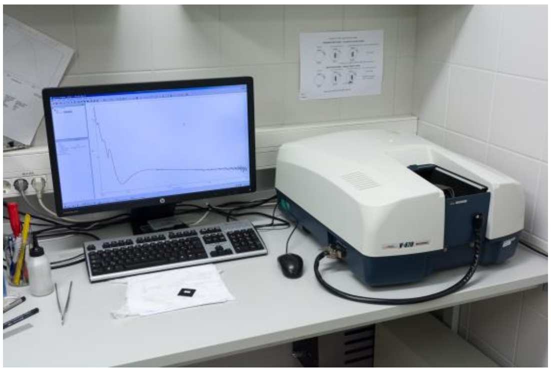
Picture 1 Picosun R200 reaction chamber on left and main computer on right. [43]

2.1.2 **Jasco, V670 optical spectrometer**

Ultraviolet visible light spectrometer (picture 2) was used to measure total transmittance and total reflectance for wavelengths of 380-1200 nm for all the samples, with reference to air. This wavelength was chosen in order to include visible light spectrum and major share of suns irradiance. For few of the samples also 290-380 nm data was collected to see impact of encapsulation in UVA and UVB region. Total transmittance and total reflectance were measured for all the samples at several points excluding few cases when human error took place.

Other parameters:

- Scan speed: 1000 nm/min
- UV/Vis Band width 5 nm
- Data pitch: 5 nm
- NIR Band width: 20 nm



Picture 2 Jasco, V670 optical spectrometer [43]

2.1.3 **Rigaku smart lab X-ray diffractometer**

In x-ray diffractometer start angle was 20° and stop angle 80°, scan speed 5.0 and sampling voltage 0.02 V. During measurement samples rotated 120 revolution per minute. X-ray diffractometer used can be seen in picture 3.

Picture 3 Rigaku smart lab X-ray diffractometer [43]

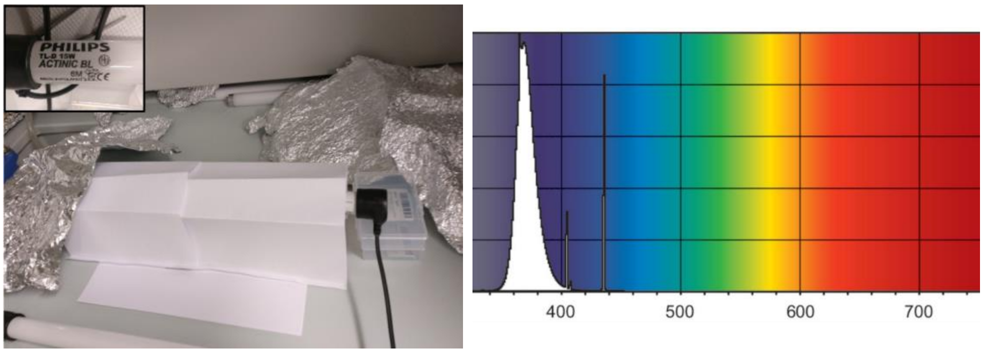
2.1.4 **Präzitherm hot plate**

Samples were annealed on the hot plate with lid closed. Samples were annealed in temperatures of 100 - 150°C for 15-30 min. (Picture 4)

Picture 4 Präzitherm hot plate

2.1.5 Philips TL-D 15W Actinic BL UV-A radiation lamp

The lamp was 6 cm away from the sample and the lamp was covered with paper and aluminum foil (picture 5). The aim of this set up was to get roughly to the same scale of intensity as sun light and to prevent UV-light from harming people working near the lamp.



Picture 5 UV exposure setup (left). The spectral power distribution of the lamp (right). [44]

Share of UV radiation in sunlight is approximately 10% of the radiation output [36] so:

$$I_{UV} = 1100\ W/m^2 * 0.1 = 110\ W/m2$$

Eventhough nominal power of the UV source is 15W the UV-A power was 3,5W according to the producer.

From this we get that light intensity at 6 cm distance is [25]:

$$I = \frac{P}{A} \qquad (1)$$

Where:
I = Light intensity
P = Power
A = Area

$$I = \frac{3.5\mathrm{W}}{4\pi * (6\ cm)^2} = \frac{0.0077\ W}{cm^2} = 77\frac{W}{m2}$$

77 W/m^2 is a little bit less than intensity of UV light from sunlight but when reflections from surrounding are considered intensity increases. Also, one of the simplifications of this calculation was to treat cylinder shape light source as point source. The purpose was not to be accurate but to be roughly in the same scale with UV irradiance of sunlight.

Samples were exposed to UV light for 30 minutes and 16h. 30min exposure was done because short photo darkening and bleaching has been noticed to improve photochromic performance of samples [45] also samples ability to bleach after short UV exposure was measured after 24h. 16h exposure was done to see the maximum photodarkening with this set up. Maximum photodarkening was also measured after annealing to see if annealing had an impact on the samples. Even though 16h exposure is rather rare to happen to actual smart windows 16h exposure can be considered as extreme conditions test to the samples.

2.1.6 **Scanning electron microscope**

SEM services were ordered from the SEM operators of TalTech. Surface and cross section pictures were taken, and film thicknesses were measured.

2.2 First experiment – Encapsulation in moderate temperature

The goal of the first measurement was to see if samples can survive encapsulation in a temperature that is slightly below ALD ideal temperature window and above YHO samples oxidation temperature.

In the first measurement sample YHO77 was deposited in ALD with Al_2O_3 in 150˚C with 300 cycles using 0.1s pulse times and 8 second purge time for TMA and 10 second purge time for H_2O. Total deposition time was 1h and 15min. After encapsulation the sample was exposed to UV-light for 30 min and left to bleach for 5 days. The photochromicity of the sample remained so it was decided that in the next measurements larger variety of deposition temperatures will be used.

2.3 Second experiment – Encapsulation using variety of temperatures

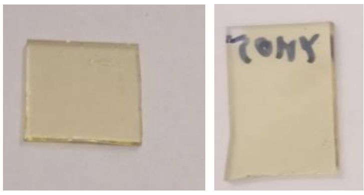
The goal of second experiment was to test different deposition temperatures and cycle amounts and see how they impact samples photochromic performance and ability to withstand annealing. Two different YHO samples were used. The samples were prepared in IFE Norway using following deposition parameters:

YHO71 (x8):

- Deposition pressure 1 Pa
- H2/Ar ratio 0.186
- Film thickness 720 nm

YHO57 (x5):

- Deposition pressure 1 Pa
- H2/Ar ratio 0.250
- Film thickness 640 nm



Picture 6 YHO71 (left) and YHO57 (right) before encapsulation, UV exposure and annealing. The difference in colour between the samples is small.

Before encapsulation with ALD samples were stored in vacuum in a storage cabinet to prevent oxidation with air. ALD deposition parameters used can be seen in table 2. When samples were put into ALD it took 30-60 min before the temperature stabilized to the deposition temperature and pulses of TMA and H_2O started.

Table 1 Sample deposition parameters.

Sample name	Stabilization time	Temperature (˚C)	Cycles	Purging (Pulse) (s)
YHO71-I-T100	30min	100	200	TMA 8 (0.1), H_2O 10 (0.1)
YHO71-I-T125	30min	125	200	TMA 8 (0.1), H_2O 10 (0.1)
YHO71-I-T150	60min	150	200	TMA 8 (0.1), H_2O 10 (0.1)
YHO71-I-T200	60min	200	200	TMA 8 (0.1), H_2O 10 (0.1)
YHO57-II-C300	30min	150	300	TMA 8 (0.1), H_2O 10 (0.1)
YHO57-II-C400	30min	150	400	TMA 8 (0.1), H_2O 10 (0.1)

The samples were named based on deposition temperature (T) or number of cycles (C). When deposition temperature was varied cycles were kept at 200 and when cycles were varied temperature was kept at 150°C. Each of the samples also had a duplicate. Purging time for 200°C is unnecessarily high and more economical option should be used if one uses ALD. Long purging time was a leftover from a plan on trying different purging times, however due to lack of time and many samples to test this plan was discarded.

It would have been better to use temperature of 100°C when depositing 300 and 400 cycles, but the UV-Vis data obtained after depositing samples in 100-150°C was inconsistent in the beginning (see more in chapter 3.2.1 Impact of temperature) and due to this temperature that worked in the first experiment (150 °C) was used.

After ALD samples went through 30 min and 16h UV-light exposure as well as 30 min annealing in 100°C. UV-Vis measurements were taken in between annealing and UV exposure as well as XRD measurements. Meanwhile some of the duplicate samples were put aside for SEM imaging and the rest were annealed without being exposed to UV-light. In the end two samples one deposited in 100 °C and one in 125 °C and annealed were sent to IFE Norway for cyclic testing. The overall testing process can be seen in more detail in appendix 1.

Four samples were sent to SEM imaging: T100, T125 (exposed to UV light and bleached), T200 and C300 (annealed). In SEM surface and cross-section were imaged and film thicknesses were measured. Few XRD measurements were also taken during the second experiment.

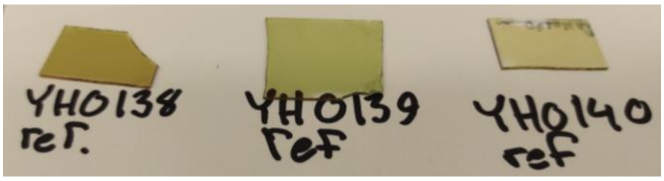
2.4 Third experiment – Encapsulation of several different samples in low temperature with Al_2O_3 and TiO_2

The goal of third measurement was to study impact of YHO samples composition to photochromic properties after encapsulation. In the second measurement it was found that depositing a sample with 200 cycles of Al_2O_3 in 100°C with purging time of 8s for TMA and 10s for water with 0.1s deposition pulse protected samples photochromic performance the best hence these deposition parameters were used.

In addition to Al_2O_3 also TiO_2 was used to encapsulate the samples since the laboratory had bought this new precursor recently. In TiO_2 encapsulation the parameters were: 300 cycles deposited in 125 °C using purging time of 3s for TiCl4 and 4s for water with 0.1s deposition pulse time. These parameters were chosen based on earlier ALD experiments done in the laboratory.

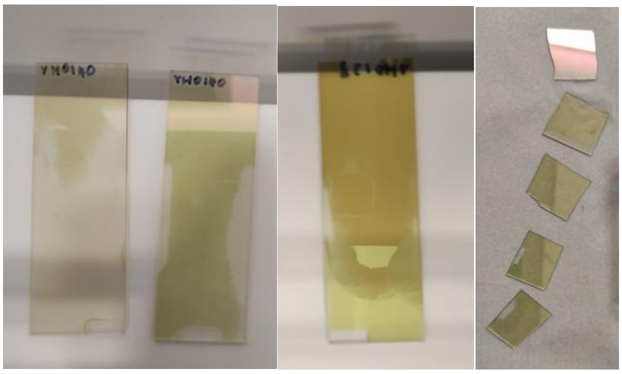
The YHO samples (picture 7) were prepared in IFE Norway with following sample names and deposition parameters:

- YHO138: deposition pressure: 0.6 Pa, H2/Ar ratio: 0.125
- YHO139: deposition pressure: 0.85 Pa, H2/Ar ratio: 0.125
- YHO140: deposition pressure: 0.25 Pa, H2/Ar ratio: 0.125



Picture 7 YHO samples before encapsulation, UV exposure and annealing.

In picture 7 it is visible that different deposition parameters have resulted in different colour of samples. Unlike samples YHO71 and YHO57 these samples were stored in desiccator. Samples YHO138-140 were stored for approximately six months before studying them due to changes in research plans. It is likely that samples YHO138-140 were exposed to air unintentionally almost constantly during the six-month storage time since it was noticed in the beginning of studies that the desiccator leaks air into it after vacuuming. Also, how well the samples were sealed for delivery in Norway may have impacted on oxidation of the samples. Delamination of the samples was visible with bare eye. (Picture 8)



Picture 8 On left two slides of YHO140 sample, in the middle YHO138 samples and on right most of the pieces of YHO139 sample. Reflections from surroundings may give false impression of delamination of YHO 139 which in reality delaminated the least.

Due to strong delamination some parts of the YHO140 samples were not used. For all the samples the measurements were taken from the middle of the sample substrates to avoid measuring delaminated parts of the samples.

There were in total four sets of YHO138-140 samples used in this measurement. One set encapsulated with Al_2O_3, one encapsulated with TiO_2, one samples set for reference and second set for reference which went through annealing unlike the other reference sample set. Two sets of reference samples were used so that in the end of studies both annealed and not annealed samples could be sent to cyclic testing in Norway. The sample sets were tested in following way:

First, to study photochromism TiO_2, Al_2O_3 and reference sample were:

1. Exposed to UV-light for 30 minutes.
2. Bleached for 24 hours.
3. Exposed to UV-light for 16h
4. Bleached for 24h and then bleached further for 6-14 days.

Second, to study impact of annealing on YHO encapsulated with TiO_2, Al_2O_3 and reference sample the samples were:

1. Annealed for 30 min in 100°C.
2. Annealed for 15 min in 150°C (because the change in total transmittance and total reflectance was minimalistic even for reference samples)
3. Exposed to UV-light for 30 min.
4. Bleached for 24h
5. Exposed to UV-light for 16h
6. Bleached for 24h and then bleached further for 6-14 days.

Third, to confirm that the reference samples have not lost their photochromicity during 16h UV exposure they were both exposed to UV light for 16h for second time.

Before and after every UV-exposure and annealing, and during bleaching UV-Vis measurements were taken. XRD measurements were taken after encapsulation in ALD, after annealing and after 16h UV exposure. In the end three YHO139 samples were sent to SEM: TiO_2 and Al_2O_3 encapsulated and one annealed reference sample.

In the end of experimenting YHO140-TiO_2, YHO140-Al_2O_3 and YHO140-ANN samples were sent to SEM imaging. In SEM imaging surface and cross-section were imaged and thicknesses of the films were measured.

3 Results

Protecting YHO samples from atmosphere was successful using Al_2O_3 deposited with ALD however bleaching rate of the samples back to transparent state lowered significantly making it unsuitable for smart window applications. TiO_2 was not a suitable encapsulant due to its reactivity with YHO but different behaviour of YHO under different thin films may be an interesting field to study further in order to explain reactions that take place in YHO better.

3.1 First experiment - Encapsulation in moderate temperature with oxidation

In the first measurement Al_2O_3 was deposited on YHO without losing photochromic properties of YHO. However, bleaching was very slow and optical properties changed during encapsulation. In figure 19 UV-Vis spectrums of the sample can be seen before and after encapsulation.

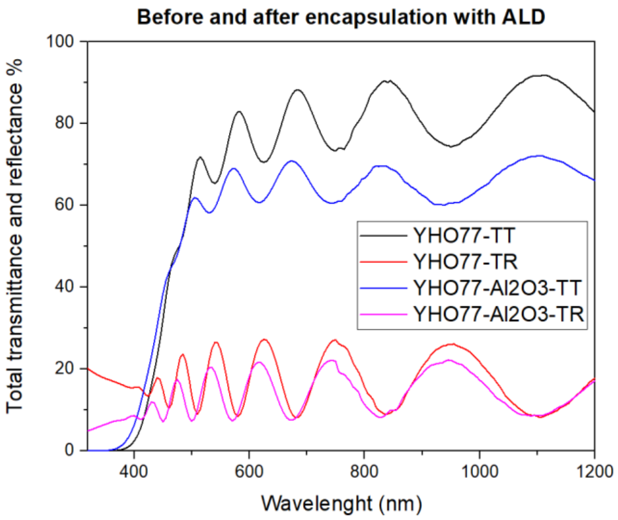
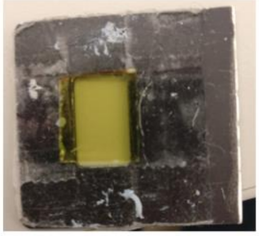


Figure 19 Total transmittance and reflectance before and after encapsulation with ALD

UV-Vis measurement was done before and after encapsulation and from the total transmittance results (figure 19) it can be seen that total transmittance % has decreased which could be due to the Al_2O_3 thin film on top of YHO. It can be also seen that total reflectance has decreased especially in the ultraviolet range due to Al_2O_3.

In picture 9 the sample can be seen after encapsulation, after 30 min UV exposure and after 5 days bleaching. The photochromic effect remained on the sample, but the bleaching was slow.

24h After encapsulation	After 30 min UV exposure	After 5 days bleaching
		

Picture 9 Pictures of the samples after encapsulation, exposure to UV light and 5 days of bleaching.

In picture 9 in box "After 5 days of bleaching" it can be seen that there are areas that have bleached more than most of the sample. This could be due to unintentional scraping of the sample that has removed Al_2O_3.

3.2 Second experiment - Encapsulation at low temperature with low oxidation

During the second experiment it was found that that deposition temperature of 100°C causes the least oxidation on the sample and gives uniform Al_2O_3 thin film. The problem with the long bleaching time remained (figure 20). The higher number of cycles caused more oxidation and no significant improvement in the quality of encapsulation was noticed (figure 21).

3.2.1 UV-Vis - Impact of temperature

The photodarkening of the samples decreased with increasing ALD deposition temperature. In figure 20 at phase where samples were exposed to UV-light for 16h it can be seen that sample deposited at 200°C has almost no photochromicity left whereas samples deposited at 100°C had even greater of film contrast than the reference sample (YHO71) that may have oxidised in air and during 16h UV exposure.

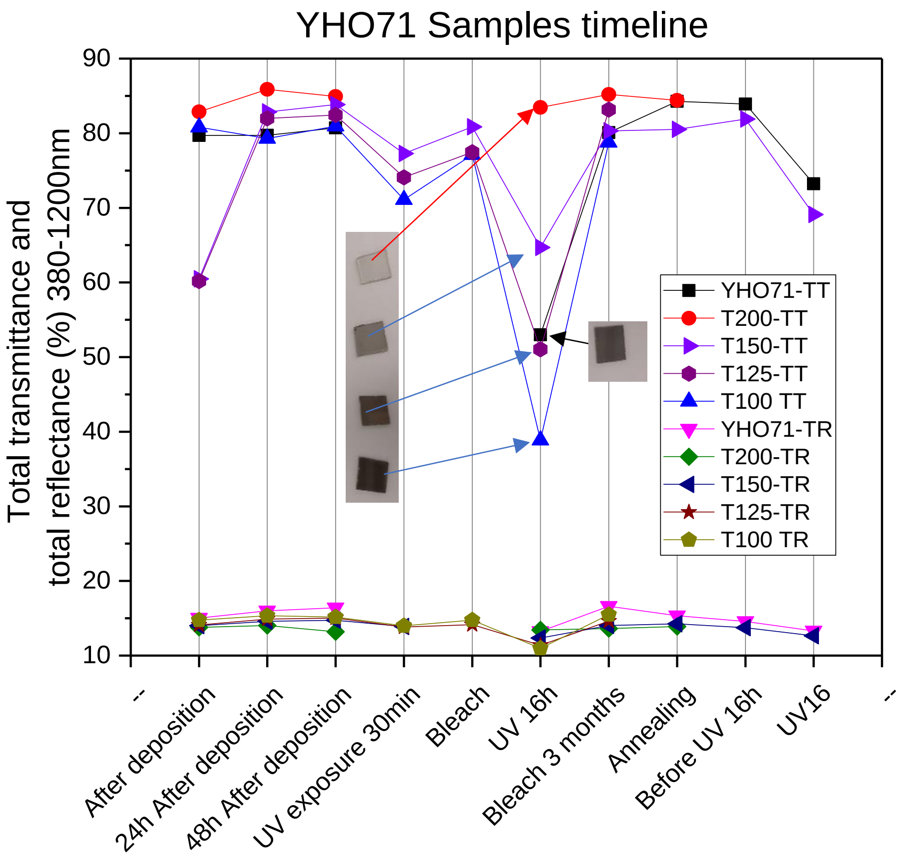


Figure 20 Average total transmittance (above) and total reflectance (below) of samples after deposition, UV-light exposures, annealing and during bleaching.

In figure 20 and 21 it can be noticed that straight after deposition some of the samples gave noticeably lower total transmittance values than others. This has most likely occurred just because there was a debris in front of the light sources or sensors inside of the UV-Vis measurement tool. However, samples T100-150 were deposited on day 1 of the experiment and samples T200,C300 and C400 on day 2 of the experiment and this deviation of total transmittance exclusively happened to samples that were measured after ALD and occurred during on two days.

3.2.2 **UV-Vis - Impact of amount of cycles**

Increasing the number of cycles did not bring noticeable difference to the performance of the films. More cycles in ALD lead to longer deposition time of the samples in elevated temperature which lead to more oxidation. Better results would have been obtained by using deposition temperature of 100°C but due to inconsistent results from UV-Vis on the first deposition day (deposition of T100-T150 samples) this was not realised and temperature of 150°C was used since it had worked during the first experiment.

In figure 21 the samples that were relevant to study impact of number of cycles are shown. T150 sample in the figure is used to represent a sample with 200 cycles of Al$_2$O$_3$ deposited on it. The comparability of T150 is not ideal since Al$_2$O$_3$ deposition was done on YHO71 samples whereas others are deposited on YHO57 samples.

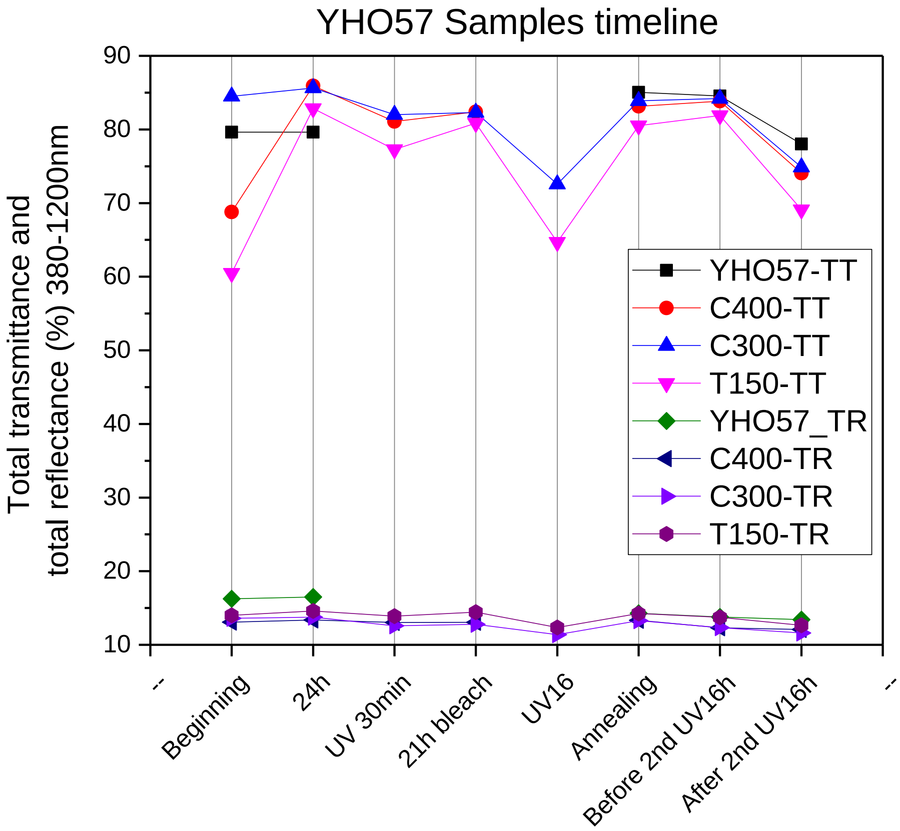


Figure 21 Average total transmittance and total reflectance of samples after deposition, UV-light exposures, annealing and during bleaching.

As figure 21 depicts there is no significant difference in performance of C300 and C400 samples. T150 sample performs better than C300 and C400 samples but this is also due to the fact that YHO71 sample is used instead of YHO57.

3.2.3 **Results from XRD**

XRD spectra indicated peak shift towards higher angles for samples that have been deposited in higher temperature (T100-T200) or for longer period of time (C300,C400) (figure 22). This is contrary to what was found in the study of You C. et al [26].

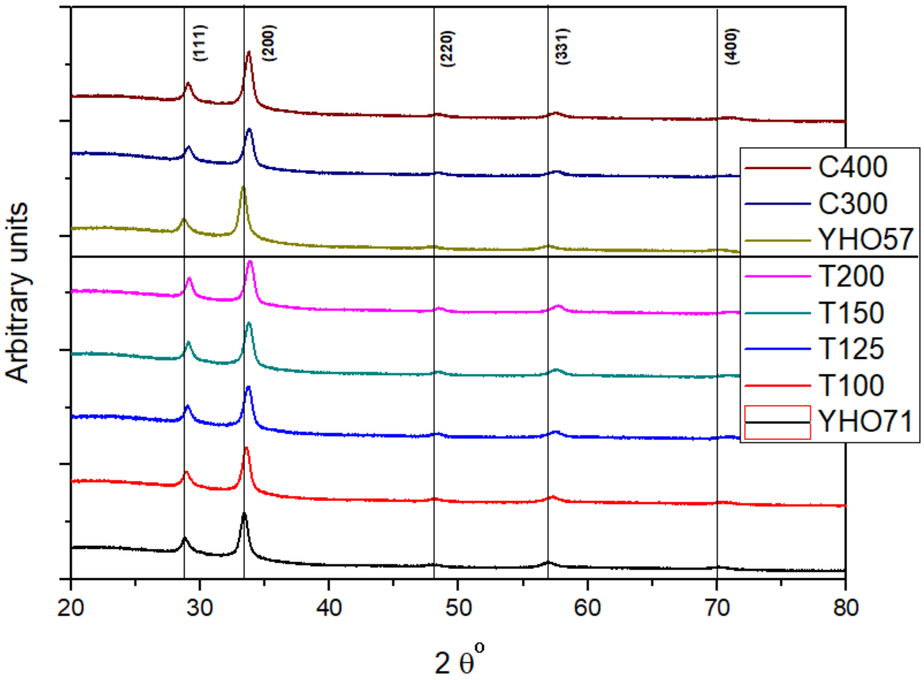


Figure 22 XRD spectra of the samples in the study. Some of the samples have gone through annealing and UV exposure before XRD measurements.

The peak shift towards larger angles means that the distance between atoms is decreasing which rather suggests loss of oxygen rather than hydrogen. Possibly both oxygen and hydrogen are being lost since in chapter 3.2.1 Impact of temperature it was shown that the photochromic performance of samples got worse as the deposition temperature increases.

3.2.4 **Results from SEM – Accelerated film growth**

The results from SEM suggest accelerated film growth. GPC of Al_2O_3 is over 1å/cycle on average for all of the samples and the higher the temperature the faster the growth is as can be seen in table 3.

Table 2 Results from SEM images.

Sample	Al_2O_3 film thickness (nm)	GPC (å/cycle)	YHO film thickness (nm)

YHO71 T100	16, 25	0.8-1.3	720
YHO71 T125	17, 29, 28	0.9-1.5	720
YHO57 C300	34, 38	1.1-1.3	640
YHO71 T200	22, 31	1.1-1.5	720

Even the samples deposited in temperature of 100°C had a uniform layer of Al_2O_3 on top of it. The fact that the surface shapes of YHO are still visible after encapsulation with ALD demonstrates the accuracy of the deposition with ALD. (Image 1)

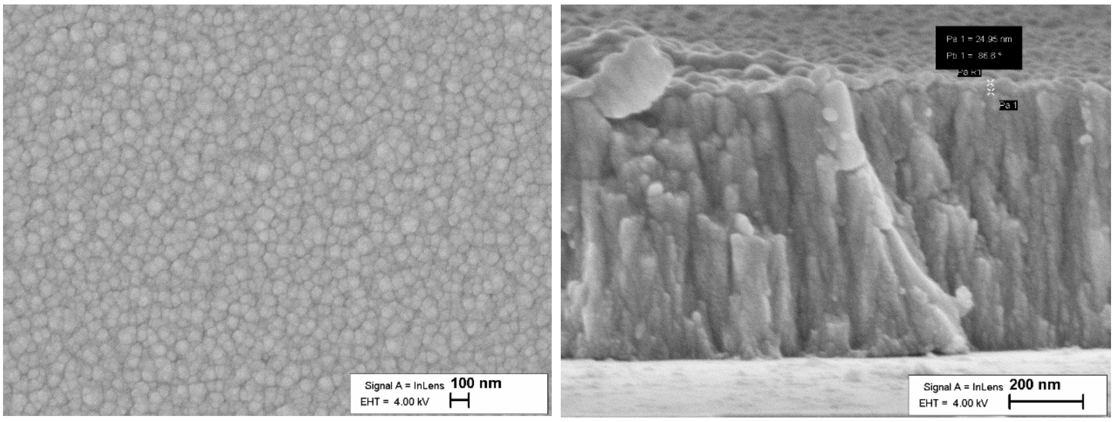


Image 1 Surface (left) and cross-section (right) of YHO71-T100 sample.

Results from cyclic testing

In cyclic testing in IFE Norway YHO71-T100 samples total transmittance in 650-850 nm range decreased by approximately 20 % point in one hour, which is moderately good result. For YHO-T125 (annealed) total transmittance decreased only 7% but bleaching was slightly slower. As it can be seen in figure 23 the bleaching back to transparent state is very slow. The samples bleached around 5% points in 5 hours.

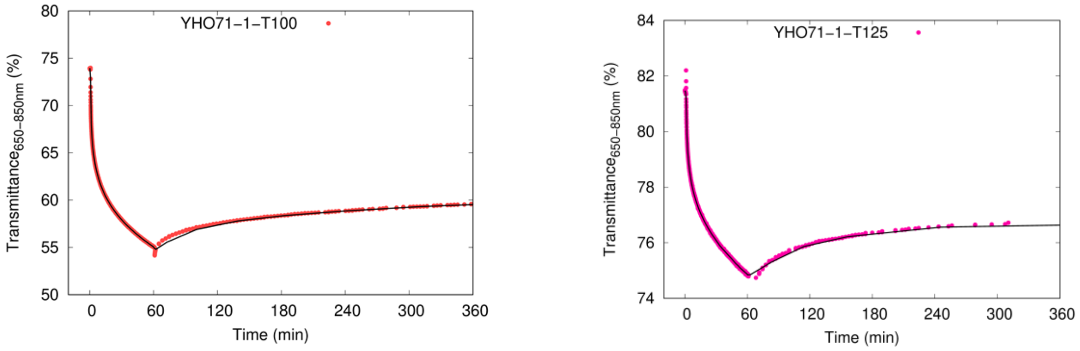


Figure 23 Cyclic testing of YHO71-T100 and YHO-T125.

More accurate analysis on bleaching rate was done by Baba E.M. using decay approach which assumes that photodarkening of YHO is the photoinduced metallic domain formation [12] therefore bleaching could be approached as "decay" of those domains, which is considered to happen through oxidation [10]. Based on the analysis the total half-life of bleaching sample YHO-T100 is 22h and sample YHO-T125 10h which is not practical if smart window applications are considered. Slow bleaching could happen because YHO is unable to "breath" oxygen as Baba E.M. et al suggested in publication *Light-induced breathing in photochromic yttrium oxyhydrides*. [10]

3.3 Third experiment - Differences between Al_2O_3 and TiO_2 encapsulation

3.3.1 **UV-Vis – TiO_2 poor encapsulant for YHO**

In figure 24 are the averages of total transmittance and total reflectance measurements at different points of the experiment for sample YHO140. Corresponding figures for YHO138 and YHO139 can be seen in appendix 2. For samples YHO139 and YHO138 in the beginning it seems like TiO_2 could be a good encapsulant since it does not have long bleaching time like Al_2O_3 has. However, after annealing and second 16h UV exposure it can be noticed that TiO_2 sample was not able to photodarken as much as other samples which defeats the benefit of fast bleaching.

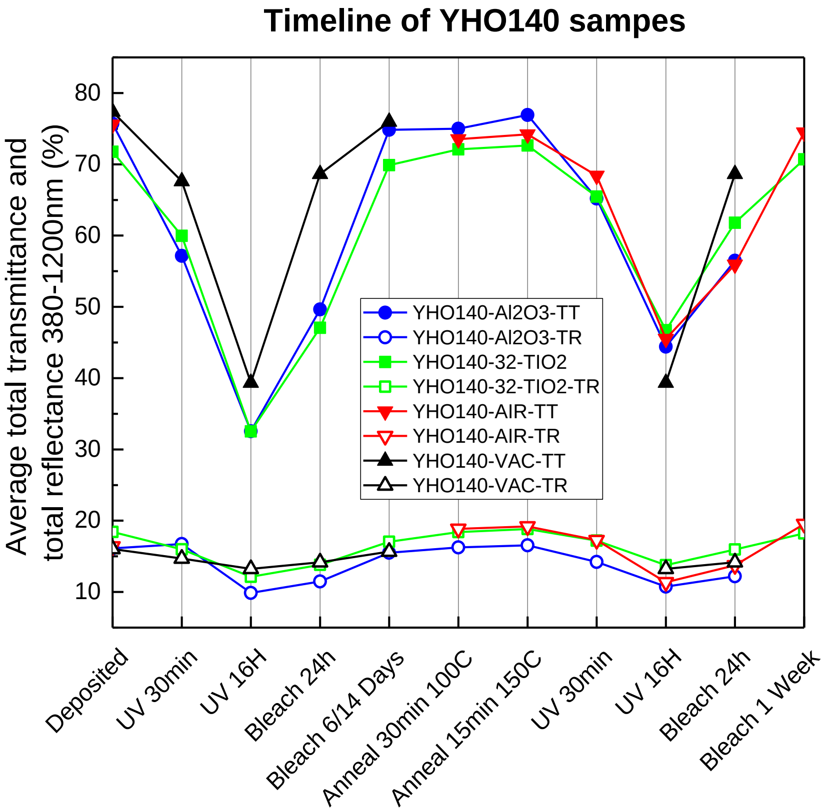


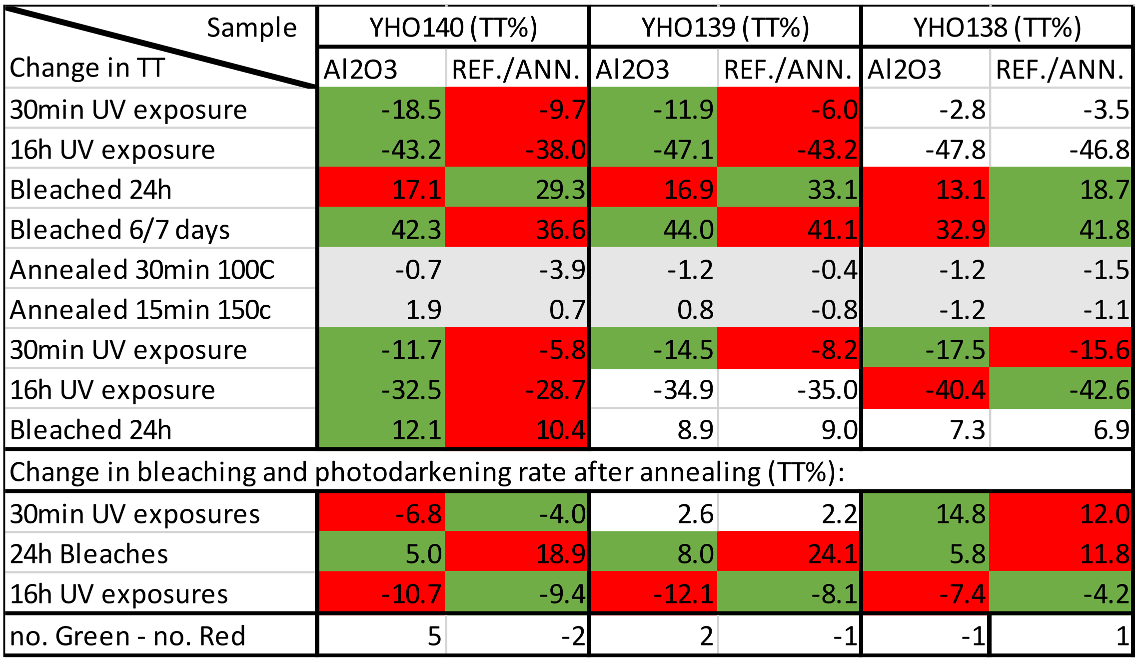
Figure 24 Average total transmittance 380nm-1200nm (%) values at different points of the experiment.

As already seen in the results of first and second experiment Al_2O_3 has slower bleaching rate than unencapsulated samples. However, after annealing the unencapsulated sample YHO139-ANN also loses its ability to bleach fast. Reaction in YHO after annealing in 150˚C seems to have taken place. This change might either prevents hydrogen and oxygen mobility in lattice or prevents YHOs interaction with air.

The degradation of photochromic performance of YHO sample encapsulated with TiO_2 might happen due to reaction between YHO and TiO_2 initiated by UV-light exposure. However, the level of photodarkening after the first 16h UV-light exposure is very similar for Al_2O_3 encapsulated. One could assume that if there is a reaction between YHO and TiO_2 initiated by UV-light it would be visible already during the first 16h UV-exposure not only after the second one. Which could mean that the reaction is initiated by annealing or combination of UV exposure and annealing. This could be confirmed by exposing TiO_2 to UV repeatedly without annealing in between.

In table 3 comparison between Al_2O_3 samples and their reference samples is shown (TiO_2 not included due to reactivity with YHO). The table is based on the same UV-Vis data that is also shown in figure 24 and appendix 2. The purpose of the comparison table was to determine whether performance of the samples improved of not in comparison with its reference sample.

Table 3 Comparison table of encapsulated samples and their reference samples based on changes in TT after each treatment and change in TT after annealing. Better performance is highlighted with green and worse with red. If difference between performance is less than 1% points there is no highlighting also results after annealing were left out. Negative values in the table mean that film has darkened and positive values that film has bleached, except in the lower part of the table where positive numbers mean that photodarkening has improved or that bleaching has slowed down.



Sample	YHO140 (TT%)		YHO139 (TT%)		YHO138 (TT%)	
Change in TT	Al2O3	REF./ANN.	Al2O3	REF./ANN.	Al2O3	REF./ANN.
30min UV exposure	-18.5	-9.7	-11.9	-6.0	-2.8	-3.5
16h UV exposure	-43.2	-38.0	-47.1	-43.2	-47.8	-46.8
Bleached 24h	17.1	29.3	16.9	33.1	13.1	18.7
Bleached 6/7 days	42.3	36.6	44.0	41.1	32.9	41.8
Annealed 30min 100C	-0.7	-3.9	-1.2	-0.4	-1.2	-1.5
Annealed 15min 150c	1.9	0.7	0.8	-0.8	-1.2	-1.1
30min UV exposure	-11.7	-5.8	-14.5	-8.2	-17.5	-15.6
16h UV exposure	-32.5	-28.7	-34.9	-35.0	-40.4	-42.6
Bleached 24h	12.1	10.4	8.9	9.0	7.3	6.9
Change in bleaching and photodarkening rate after annealing (TT%):						
30min UV exposures	-6.8	-4.0	2.6	2.2	14.8	12.0
24h Bleaches	5.0	18.9	8.0	24.1	5.8	11.8
16h UV exposures	-10.7	-9.4	-12.1	-8.1	-7.4	-4.2
no. Green - no. Red	5	-2	2	-1	-1	1

The comparison table depicts that encapsulation improves resistance to annealing in 150˚C of samples YHO140 and YHO139 (if bleaching and photodarkening are given equal value.) In the case of YHO138 the encapsulated sample performs worse than unencapsulated. However, this comparison does not consider that what matters is the balance of bleaching rate and photodarkening not performing well in just one of them.

Before UV exposure YHO138 had total transmittance of 68%, YHO139 74% and YHO140 77%. This suggests that samples with lower total transmittance (and lower oxygen content) are more resistant to elevated temperature without encapsulation but if one wants to produce a glass that is clearer and is willing to compromise the bleaching rate encapsulation with Al_2O_3 can be done. Also, refractive index of Al_2O_3 is approximately 1.5 and refractive index of YHO is 2.3 thus Al2O3 encapsulation can suppress light reflection from window.

3.3.2 XRD results – Using different encapsulants to learn about photochromicity of YHO

Even though results from UV-Vis showed us that TiO_2 is not a suitable encapsulant for YHO this can help in learning more about what king of reactions are taking place inside of YHO during UV-light exposure and annealing. What reactions take place between YHO and TiO_2 that causes rapid degradation of photochromic performance and are these reactions cause by UV-light and/or annealing? The lattice contractions and expansions recorded as peak shifts in XRD as well as change in share of different bond lengths recorded as changes in peak intensity in XRD can give a hint about atoms that leave the film and reconstructions of crystal lattice that take place. XRD patterns from 2θ angles 20-80 were collected but only angles 27-35 were analysed since the peaks in this range have the clearest response to UV light and annealing. XRD patterns can be seen in appendices 3-5.

Appendix 3 XRD results from third experiment: After encapsulation shows that both TiO_2 and Al_2O_3 encapsulated samples have slight peak shift toward right but surprisingly intensity increases for TiO_2 film and decreases for Al_2O_3 film. Right ward peak shift in the graphs indicate contraction that can take place because of oxygen and/or hydrogen release from the films. Enhancement of intensity might be related to reflection from certain crystallographic plane which is unexpected since the material is polycrystalline. In low temperature deposition with ALD amount of hydrogen impurities increases (figure 13) but if that can alone cause such difference in XRD patterns is unlikely. TiO_2 was deposited in temperature of 125°C and Al_2O_3 in 100°C which can explain oxidation of TiO_2, on the other hand Al_2O_3 sample spent more time in ALD due to longer purging times. The most curious about these changes is the fact that their impact on maximum photodarkening was rather low. The difference in maximum photodarkening of YHO139 samples was roughly 8% (TT) and for YHO138 only 2% (TT). TiO_2 and Al_2O_3 themselves should be amorphous hence not visible in XRD patterns also 17-30nm encapsulation layer should not show much on top of hundreds of nm of YHO.

Appendix 4 XRD results from third experiment: After 16h UV-light exposure shows that all the samples have decrease in peak intensity, but the change tends to be stronger for the reference samples and annealed reference sample. Since all the samples experienced similar levels of photodarkening but still have different crystal structure shows that photodarkening does not require contact with air but the bleaching process is significantly impacted by the atmosphere as it has been shown in earlier studies and publications on YHO such as recently published *Temperature-Dependent Photochromic Performance of Yttrium Oxyhydride Thin Films* by Baba E.M. et al. [46] In addition to confirming earlier findings, it could be suggested that after Al_2O_3 deposition the oxide rich surface on top of YHO changes which can be seen as drop in the intensity of peak (200).

Appendix 5 XRD results from third experiment: After annealing in 100˚C for 30 minute and in 150 ˚C for 15 min shows peak shift rightwards for all the samples and lowering in peak intensity, excluding YHO138-TiO_2 sample. YHO140 Experiences more distinguishable peak movement than rest of the samples this could be due to delamination of the samples in elevated temperature that will be further introduced in the SEM results.

3.3.3 SEM results of YHO140 samples: differences in delamination

The SEM results from YHO140 samples showed different levels of delamination for films (image 3) and different growth rates for TiO_2 and Al_2O_3 (table 4). The growth rate of TiO_2 was roughly 1 å/cycle and GPC of Al_2O_3 was 0.7-0.9 which is lower than the results gained for samples YHO71 and YHO57 earlier. The reason for this could be the fact that films has been measured from only a few points and more measurement points would provide more accurate results, also the fact that deposition has been made in low temperature plays a role.

Table 4 SEM results and GPC of TiO_2 and Al_2O_3

Sample	Thickness of encapsulating layer (nm)	Growth per cycle (å/cycle)	YHO film thickness (nm)
YHO140-TiO_2	31, 35	1-1.2	774
YHO140-Al_2O_3	19, 22	0.7-0.9	774
YHO140-ANN	-	-	721

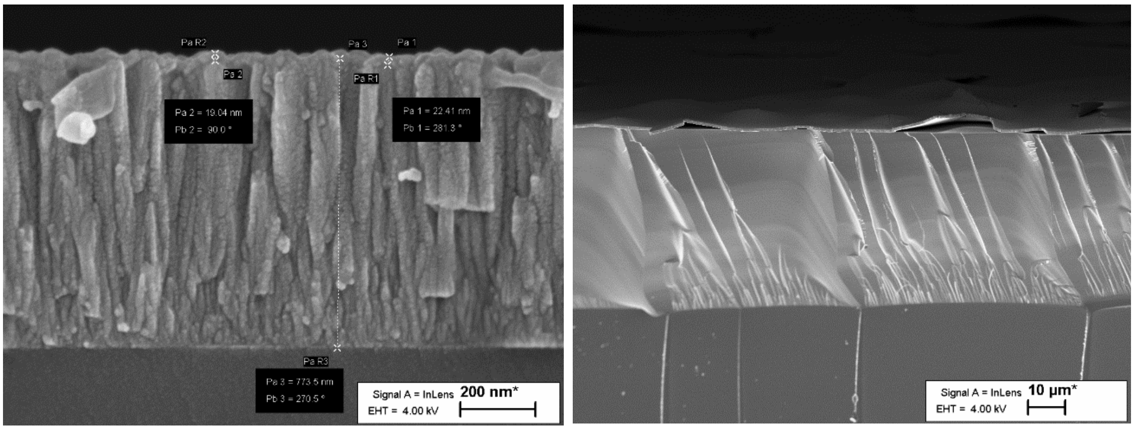


Image 2 Cross-section of Al_2O_3 film with film thicknesses (left) and cross-section of annealed YHO140 film showing delamination (right)

GPC of TiO_2 was 1 Å/cycle which is like the findings of W. Chiappim et al [32]. Based on SEM images YHO films had consistent thickness.

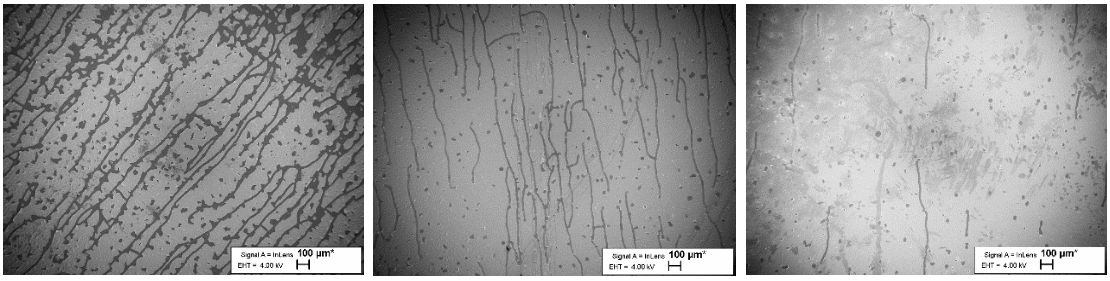


Image 3 SEM images of delamination. Left annealed, center TiO_2, right Al_2O_3

Delamination of YHO seems to depend on the material that has been used to encapsulate it. Image 3 depicts that nonencapsulated sample delaminates the most, TiO_2 improves resistance to delamination moderately and Al_2O_3 prevents delamination the best but does not seem to fully prevent it. Some of the delamination of the samples may have happened before encapsulation due to long storage time.

3.3.4 **Results from cyclic testing**

The results from cyclic tests (figure 25) show somewhat similar results to the ones gathered during UV exposures and UV-Vis measurements. However TiO_2 encapsulated sample seems to behave the same as Al_2O_3 encapsulated and annealed samples eventhough the results shown in figure 24 and appendix 2 suggest that TiO_2

encapsulated sample bleaches faster than Al_2O_3 encapsuated. Figure 24 and appendix 2 however only shows the type of bleaching that takes place after 16h UV exposure so it could be that the bleaching is faster only when the sample has been photodarkened to its limits. Also the UV-lamp used in 16h UV-exposure and in cyclic testing may have different intensities or wavelenght regions.

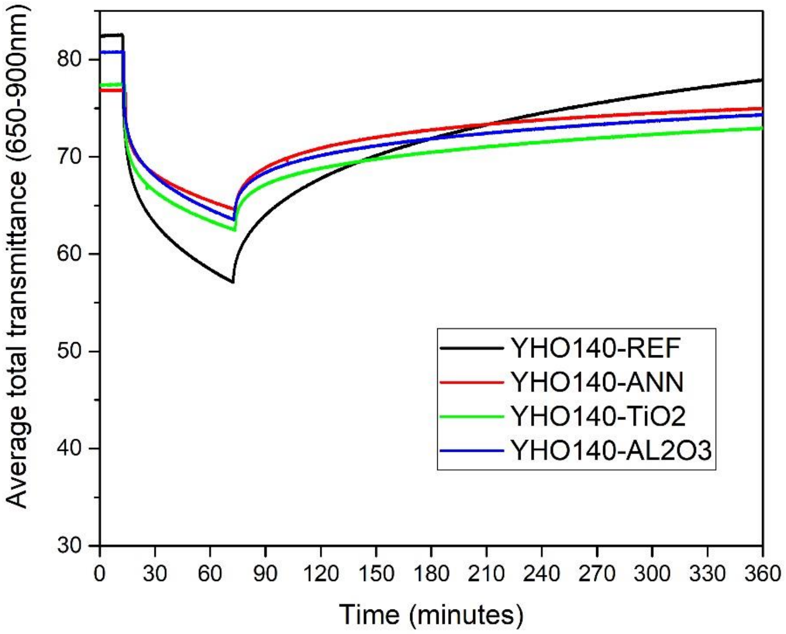


Figure 25 Results from cyclic testing of different YHO140 samples

In figure 26 it appears as if YHO138-Al_2O_3 is the best performing sample out of the samples that have been encapsulated with Al_2O_3. It photodarkens 30% points while other samples darken approximately 15-20% points however longterm bleaching is not shown in the figure and as table 3 shows the long term bleaching of YHO138 is slower than the one of YHO139-Al_2O_3 and YHO140-Al_2O_3.

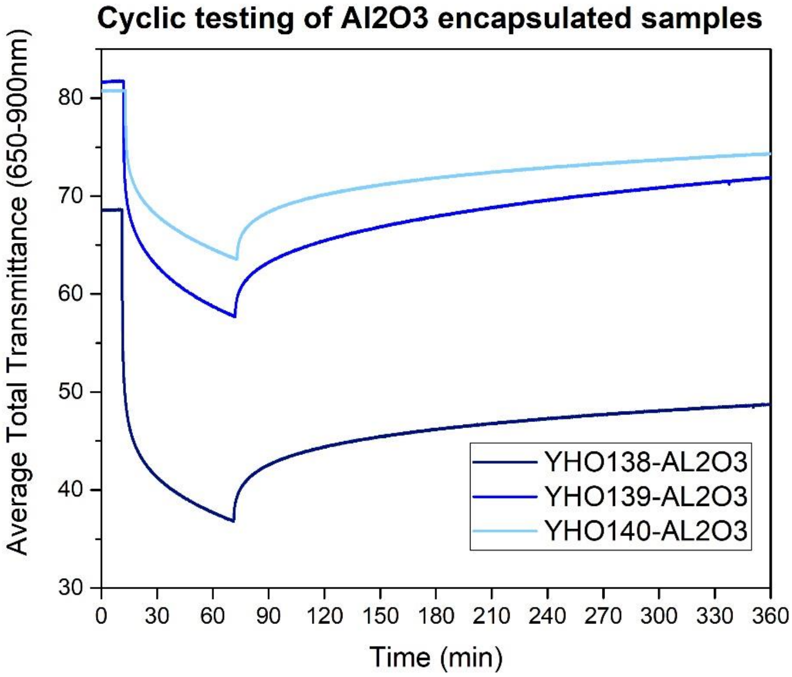


Figure 26 Results from cyclic testing of YHO138-140 sample encapsulated with Al_2O_3.

SUMMARY

Yttrium oxyhydride is a fascinating compound that has potential to function as a photochromic material in smart glass applications. The complexity of the compound however makes it challenging to understand what kind of reactions are taking place inside the crystal structure. Also, predicting behaviour in different kind of conditions is challenging which brings uncertainty to the long-term reliability of the compound. One way to bring certainty to the long-term performance is encapsulation of the material which however may have negative impact on bleaching time, as this study confirmed.

In this thesis atomic layer deposition, a state-of-the-art low temperature thin film deposition method, was used to encapsulate YHO with Al_2O_3 and TiO_2. Temperatures between 100-200°C were used to deposit films with thickness of 20-40nm on five different YHO samples with different kind of optical properties. After encapsulation samples were exposed to elevated temperatures of 100-150°C and UV light exposures with length of 30 minutes and 16 hours.

The testing methods used were not ideal if one wants to exactly know how YHO behaves when used as smart window in atmospheric conditions. However, if samples can survive short term in extreme conditions, one can expect good performance also in atmospheric conditions. Also, the amount of time that there is to do a master's thesis calls for rapid results. The most important thing that this testing method lacks is impacts of humidity which were not tested at all. The fact that some of the samples were exposed to air for a long time and delaminated due to contact with air brings a level of uncertainty to the results.

The results of this study state that the bleaching time of YHO suffers from encapsulation but resistance to elevated temperature improves. The properties of the YHO samples do not impact the bleaching time much if the samples are encapsulated. Encapsulation with TiO_2 has often better bleaching rate than Al_2O_3 but the ability to photodarken repeatedly lowers due to reaction initiated by UV light or/and high temperature. An attempt was made to analyse the XRD data from samples YHO138-140 but the results were very inconsistent and possibly a further study might be able to draw more knowledge from them than has been done in this research.

There were noticeable differences between different YHO samples that were used in this experiment. YHO71 and YHO57 lost their ability to photodarken after exposure to temperature of 100-150 °C whereas samples YHO138-140 kept their photodarkening rather well even though bleaching rate decreased. Due to these findings, I suggest focusing efforts on the design of YHO or if encapsulation is done, I suggest using methods that give more porous film than ALD so that YHO has better chances to breath.

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APPENDICES

Appendix 1 Workflow of second experiment

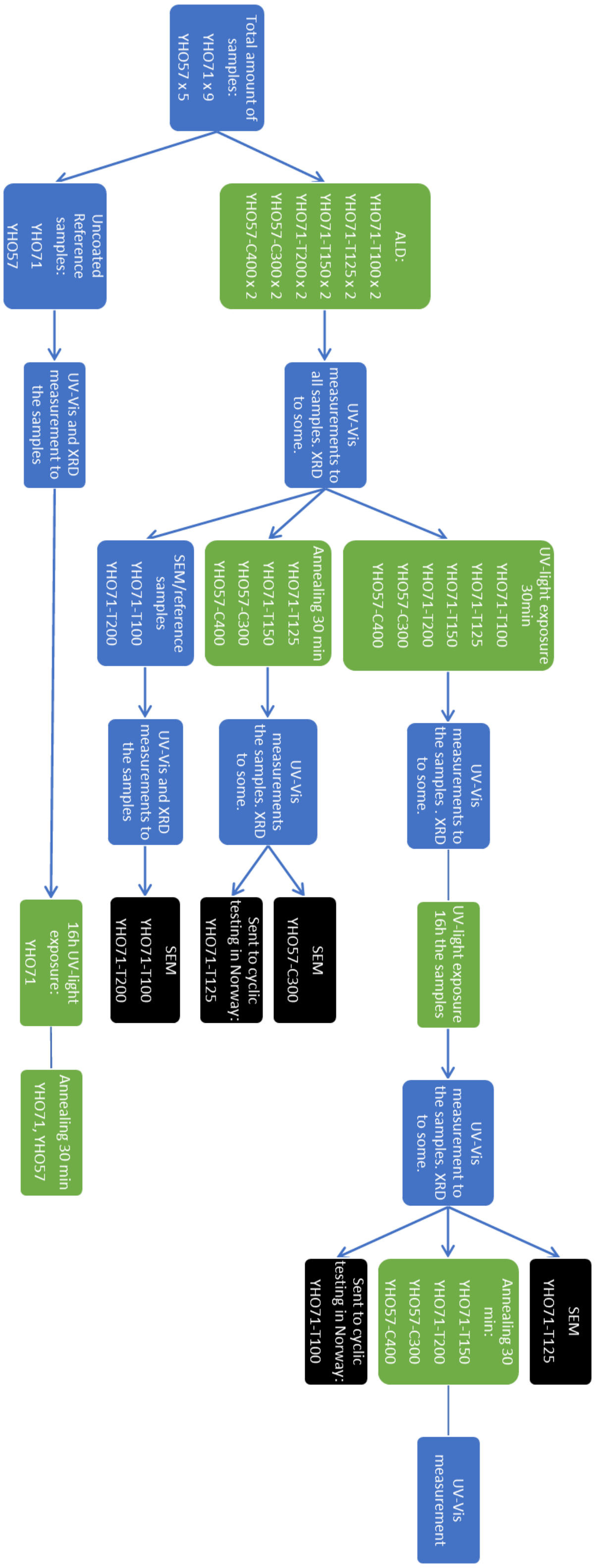
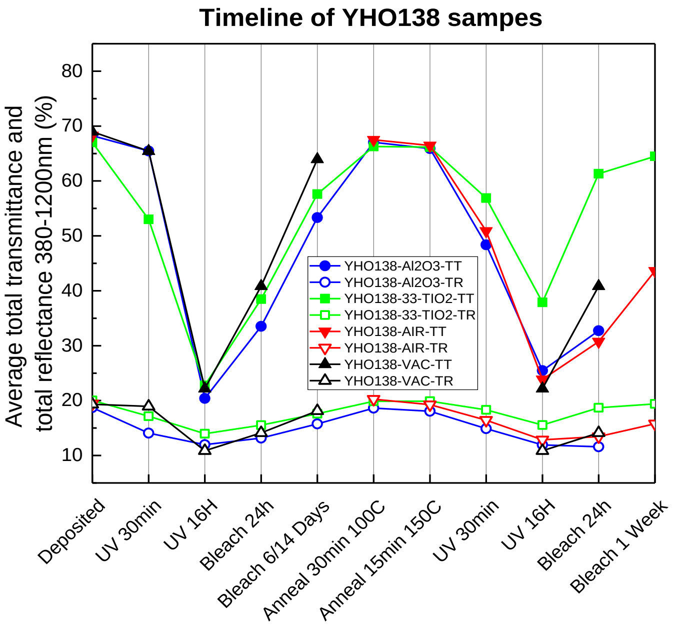
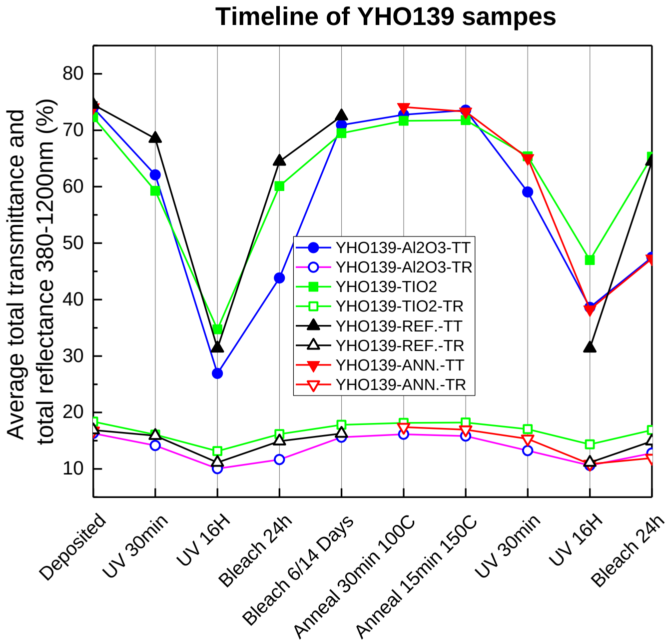


Figure 3 The overall test at phase 2. Measurements are in blue rectangles, exposure to heat or UV in green and destructive testing or sending samples to IFE in black rectangles

Appendix 2 Timelines of UV-Vis measurements from third experiment





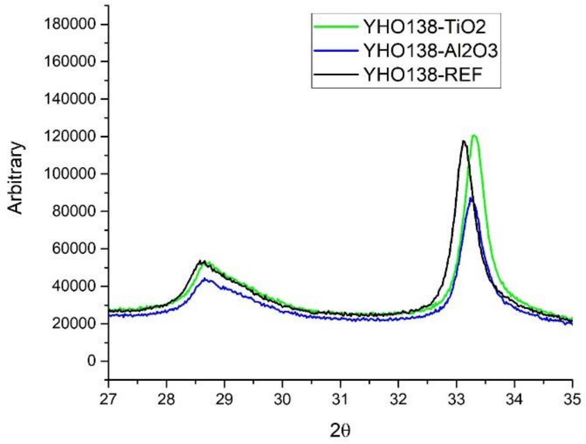
Appendix 3 XRD results from third experiment: After encapsulation

a)

Comments:

TiO_2: Intensity increases a little

Al_2O_3: Intensity decreases

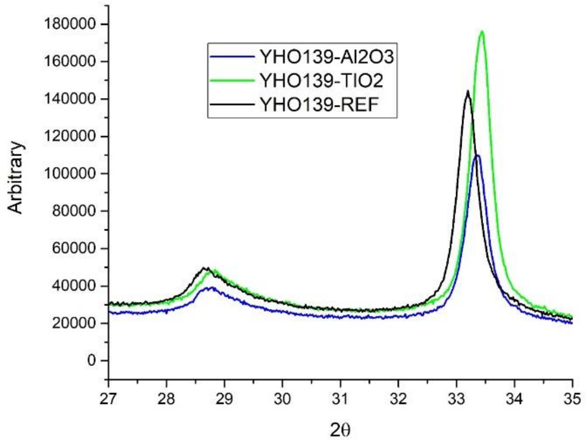


b)

Comments:

TiO_2: Intensity increases

Al_2O_3: Intensity decreases

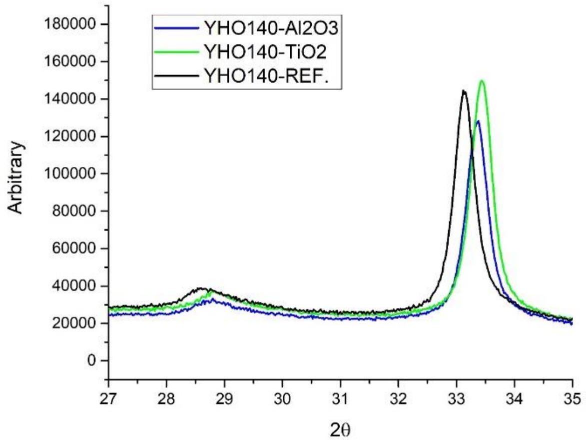


c)

Comments:

TiO_2: Intensity increases a little

Al_2O_3: Intensity decreases a little



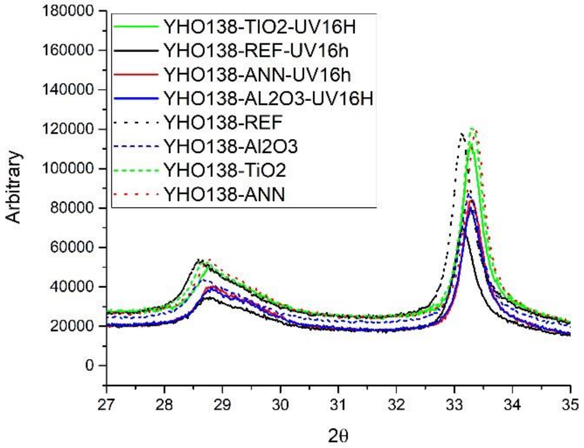
Appendix 4 XRD results from third experiment: After 16h UV-light exposure

a)

Comments:

All: Peak intensity decrease

REF and ANN: Strongest intensity decrease

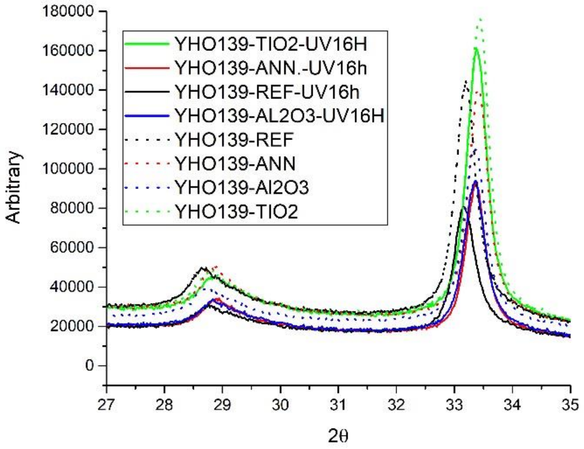


b)

Comments:

All: Peak intensity decrease

REF and ANN: Strongest intensity decrease.



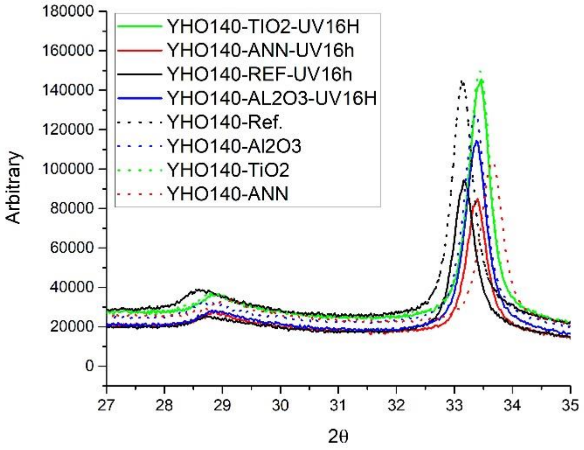
c)

Comments:

All: Peak intensity decrease

REF: Strong intensity decrease

ANN: Peak shift left



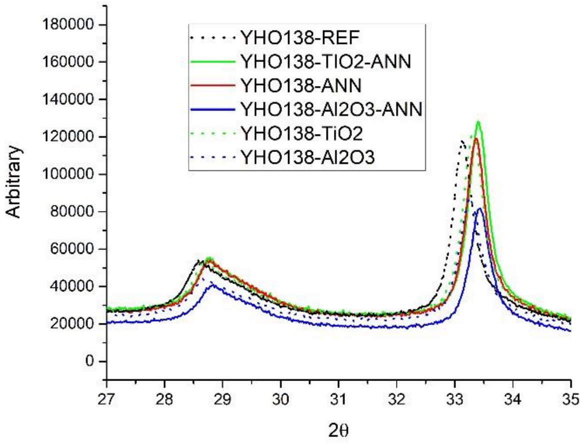
Appendix 5 XRD results from third experiment: After Annealing in 100˚C for 30 min and 150˚C for 15 min

a)

Comments:

All: Peak shift right

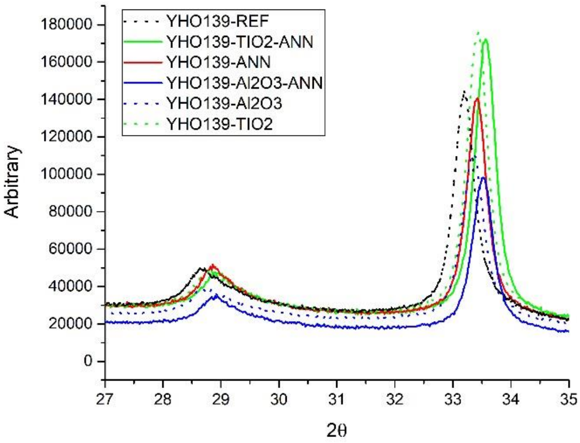
TiO_2: Intensity grows



b)

Comments:

All: Peak shift right, intensity lowers



c)

All: Peak shift right, intensity lowers

REF: Highest decrease in intensity

Behaves differently to YHO138 and YHO139. Possibly due to delamination.