ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

THIN FILM COATINGS WITH VARIOUS MATERIALS AND TECHNIQUES FOR SMART GLASS APPLICATIONS

M.Sc. THESIS

Ayşe DİCEL

Department of Nano Science and Nano Engineering

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JUNE 2021

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AKILLI CAM UYGULAMALARI İÇİN FARKLI MALZEMELER VE TEKNİKLERLE İNCE FİLM KAPLAMALAR

YÜKSEK LİSANS TEZİ

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HAZIRAN 2021

Ayşe Dicel, a M.Sc. student of İTU Graduate School student ID 513181003 successfully defended the thesis entitled "THIN FILM COATINGS WITH VARIOUS MATERIALS AND TECHNIQUES FOR SMART GLASS APPLICATIONS", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 10 June 2021
Date of Defense : 28 June 2021

To my dear mother, father and grandmother,

FOREWORD

First of all, I express my gratitude to my thesis advisors Prof. Dr. Esra ZAYİM for their support, guidance and all the opportunities they have provided to me.

Secondly, the encapsulation of photochromic YHO part of the work I would like to thank Dr. Smagul KARAZHANOV for his support and opportunities that they have provided to me during my Erasmus period. I also acknowledge Şişecam for providing electrochromic film production and characterization contribution I would like to thank Dr. Öcal TUNA and the laboratory of Şişecam vacuum coating department for providing all the facilities for magnetron sputtering of LiPON and characterization of thin films.

Finally, I would like to express the greatest gratitude to my parents and best friends for their encouragements, supports and guidance even in the most difficult times.

July 2021 Ayşe DİCEL

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ABBREVIATIONS

ALD : Atomic layer deposition
CVD : Chemical vapor deposition
DC : Direct current
ECD : Electrochromic device
ITO : Indium tin oxide
LbL : Layer by layer
LED : Light emitting diode
LiPON : Lithium phosphorus oxynitride
MBE : Molecular beam epitaxy
MOCVD : Metal organic chemical vapor deposition
PCM : Photochromic materials
PES : Pulse electrode deposition
PLD : Pulsed layer deposition
PVB : Polyvinyl butyral
PVD : Physical vapor deposition
PVP : Polyvinylpyrrolidone
RF : Radio frequency
SEM : Scanning electron microscope
UV : Ultraviolet
XRD : X-ray diffraction
YHO : Yttrium oxyhydride

SYMBOLS

sccm	**:** Standard Cubic Centimeters Per Minute
λ	**:** Wavelength (nm)
W	**:** Watt
V	**:** Voltage
eV	**:** Electronvolt
t	**:** Time
Torr	**:** Torr (101325 Pa)
n	**:** Refractive Index
nm	**:** Nanometer (10^{-9} m)
Å	**:** Angstrom (10^{-10} m)
ω	**:** Angular Velocity
T%	**:** Transmission
rpm	**:** Rotations Per Minute

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THIN FILM COATINGS WITH VARIOUS MATERIALS AND TECHNIQUES FOR SMART GLASS APPLICATIONS

SUMMARY

It is very important to create efficient energy sources in order to meet the energy need emerging with the developing technology. Thin films are structures that are coated on a substrate with a thickness of up to 1 micrometer and can be used for energy saving in many applications. Thin films are widely used in the development and functionalization of optoelectronic, photonic, magnetic and similar devices. Especially in recent years, it is possible to provide energy efficiency thanks to the partial darkening feature in building windows. Also known as thin-film solar technology, II. An unlimited number of application areas such as next-generation solar cells, chromogenic and photovoltaic applications, large building glasses, dashboards, and ease of production with both organic and inorganic materials make thin film coatings an important research topic and ensure efficient use of energy.

Chromogenic materials, which have been studied for more than fifty years, have been intensively studied by manufacturers and researchers in recent years due to the increase in their commercialization potential. Chromogenic materials are materials that change color reversibly under certain external factors. These external effects can vary as temperature, electric current, photon, pressure, mechanical stress and are called by different chromogenic names that describe this external effect. Materials that change color reversibly as a result of the application of electric current are called electrochromic materials (EC), while materials that change their optical properties with the effect of incident light according to their presence in a luminous and stable environment are called photochromic materials. It finds use in existing applications such as automotive, architecture, aircraft and device digital displays, and eyeglass lenses. We can define EC and PC glasses as active (dynamic) and passive glasses, which attract attention especially with their applications in large building glasses. While EC glasses are dynamic glasses in which the color changes in a controlled manner when a low voltage is applied, PC coated glasses are glasses that change color with the effect of light. In thin film preparation, many effects such as coating methods, starting materials used, coating parameters, interface physics affect the structural, electronic and optical properties of thin films, while also determining their functionality.

In this thesis, metal transition oxide films were coated on the glass substrate with different coating methods. In the first stage, nickel oxide, silicon oxide, aluminum oxide and titanium oxide films were coated on glass substrates of approximately the same thickness by evaporation method with a physical coating method, e-beam. Non-metallic homogeneous coatings were obtained by adjusting the coating parameters such as oxygen pressure and coating speed by e-beam evaporation method of MOx thin films. In the next step, these four metal oxides were coated separately in the range of 100-200 nm on YHO coated glass, which showed photochromic properties and was

developed by our working group. Thus, as the control group, MO_x films that we developed on YHO coated glasses were coated and its effect on PC properties was examined. Photochromic properties of YHO thin films are a newly studied subject in the literature, and YHO thin films exhibit photochromic properties at room temperature. However, the PC performance of YHO thin films is sensitive not only to photon wavelength, photon intensity, illumination time and ambient temperature, but also to humidity. Therefore, encapsulation is expected to improve PC properties. After examining the effect of MOx encapsulation, the effect of organic coatings was investigated. Using organic materials, PVB and PVP polymers were coated on YHO coated glasses with the spin coating method, which is one of the sol-gel methods. With the sol-gel method, which is a fast, low-cost and easy method, PVB and PVP polymers were homogeneously coated on YHO glass-coated films by varying the coating speed and solution concentration. In this part of the thesis, the effects on long-term optical performances of metal oxides and polymers encapsulated by coating YHO were investigated. The advantage of the electron-beam evaporation method is that more than one different material can be coated in the crucible at the same time (in-situ), providing precise film thickness. With this method, MOx was synthesized with the same coating parameters.

In the first part of the thesis, physical and chemical coatings were studied in detail and smooth, controlled thin films were synthesized and the effects of these inorganic and organic materials on PC (passive glass) properties were partially investigated. Nickel oxide and tungsten oxide thin films, which are widely used in the hole transport layer (HTL) of perovskite solar cells, are used in EC glasses, which are active glass, also known as smart glass. These materials, which have wide commercialization potential, were synthesized in the second part of the thesis by the magnetron sputtering method, which is widely used in commercial applications.

In addition, WO_3 and NiO are frequently used electrode materials in the literature due to their high stability and durability. These materials are coated on transparent conductive substrates (ITO) by magnetron sputtering method due to the necessity of the application areas mentioned above. Thus, both NiO and WO_3 were successfully coated with different coating methods on substrates with different physical properties. In the last stage of the thesis, LiPON (lithium phosphorus oxy nitride), which is used as electrode material in fuel cells and EC devices, is coated as a solid electrolyte on silver electrodes by magneton sputtering method and its characterizations have been made.

In summary, NiO, Al_2O_3, SiO_2, TiO_2 thin films were coated on glass substrates by e-beam evaporation method and PVB, PVP polymers were coated with sol-gel method. NiO and WO_3 thin films were coated on ITO coated glass substrates by spraying method. In the final stage, LiPON was coated on silver electrodes. Thin films, which find a wide application area, have been successfully coated on different substrates.

AKILLI CAM UYGULAMALARI İÇİN FARKLI MALZEMELER VE TEKNİKLERLE İNCE FILM KAPLAMALAR

ÖZET

Gelişen teknolojiyle açığa çıkan enerji ihtiyacını karşılamak için verimli enerji kaynaklarının yaratılması çok önemlidir. İnce filmler en fazla 1 mikro metre kalınlığında bir altlık üzerine kaplanan yapılardır ve birçok uygulamada enerji tasarrufu amacıyla kullanılabilirler. Optoelektronik, fotonik, manyetik ve bunun gibi cihazların geliştirilmesinde ve fonksiyonlaştırılmasında ince filmlerin kullanım alanları çok geniştir. Özellikle son yıllarda bina camlarında kısmi kararma özelliği sayesinde enerji verimliliği sağlamak mümkündür. İnce film güneş teknolojisi olarak da bilinen II. nesil güneş hücreleri, kromojenik ve fotovoltaik uygulamalar, büyük bina camları, gösterge panoları gibi sınırsız sayıda uygulama alanları ve hem organik hem inorganik malzeme ile üretim kolaylığı ince film kaplamaları önemli bir araştırma konusu haline getirirken enerjinin de verimli olarak kullanılmasını sağlamaktadır.

Elli yılı aşkın süredir çalışılan kromojenik malzemeler, son yıllarda ticarileşme potansiyellerinin artması sebebiyle özellikle üretici firmalar ve araştırıcılar tarafından yoğun olarak çalışılmaktadır. Kromojenik malzemeler belirli dış etkenler altında tersinir olarak renk değiştiren malzemelerdir. Bu dış etkiler sıcaklık, mekanik stres, çözücü polaritesi, biyokimyasal ve hidroliz reaksiyonları olarak değişebilir ve sırasıyla termokromizm, mekanokromizm, solvatokromizm, kemokromizm ve biyokromizm olarak adlandırılır. Elektrik akımı uygulanması sonucu tersinir olarak renk değiştiren malzemelere elektrokromik malzemeler (EC) denirken, aydınlık ve kararlık ortamda bulunma durumuna göre gelen ışığın etkisi ile optik özelliklerin değiştiren malzemelere fotokromik malzemeler olarak adlandırabiliriz. Özellikle otomotiv, mimari, uçak ve cihazların dijital ekranları, gözlük camı gibi mevcut uygulamalarda kullanım alanı bulmaktadır. Özellikle büyük bina camlarındaki uygulamaları ile dikkat çeken EC ve PC camları aktif (dinamik) ve pasif camlar olarak tanımlayabiliriz. EC camlar düşük bir gerilim uygulandığında kontrollü olarak rengin değiştiği dinamik camlarken, PC kaplı camlar ışığın etkisi ile renk değiştiren camlardır. İnce film hazırlamada, kaplama yöntemleri, kullanılan başlangıç malzemeleri, kaplama parametreleri, ara yüzey fiziği gibi pek çok etki ince filmlerin yapısal, elektronik, optik gibi özelliklerini etkilerken, işlevselliğini de belirlemektedir.

Bu tez çalışmasında, farklı kaplama yöntemleri ile metal geçiş oksit filmler cam altlık üzerine kaplanmıştır. İlk aşamada fiziksel bir kaplama yöntemi olan electron demeti ile buharlaşma yöntemi ile nikel oksit, silisyum oksit, alüminyum oksit ve titanyum oksit filmleri yaklaşık aynı kalınlıkta cam altlıklar üzerine kaplanmıştır. MOx ince filmleri elektron demeti buharlaştırma yöntemiyle oksijen basıncı, kaplama hızı gibi kaplanma parametrelerini ayarlayarak metalik olmayan homojen kaplamalar elde edilmiştir. Daha sonraki aşamada fotokromik özellik gösteren ve çalışma grubumuz tarafından geliştirilen YHO kaplı cam üzerine bu dört metal oksit ayrı ayrı 100-200 nm aralıklarında kaplanmıştır. Kaplama hızı, oksijen basıncı, kalınlık gibi

parametreler optimize edilip YHO üzerine homojen ve fotokromik özelliklerin çıplak gözle görülebildiği enkapsülasyonlar yapılmıştır. Her metal oksit için ayrı ayrı optimizasyon çalışmaları yapılmıştır ve sonucunda hepsinde istenen homojen yapı elde edilmiştir. YHO tarafından sağlanan fotokromik özelliğin enkapsülasyon sonrasında da gözle görünür bir şekilde devamlılığı sağlanmıştır. Böylece kaplama konusunda elde ettiğimiz tecrübeyi kontrol grubu olarak YHO kaplı camlar üzerine geliştirdiğimiz MOx filmler kaplanarak PC özellikleri üzerine etkisi incelenmiştir. YHO ince filmlerinin fotokromik özellikleri literatürde yeni çalışılan bir konu olup YHO ince filmler oda sıcaklığında fotokromik özellikler sergilemektedir. Bununla birlikte, YHO ince filmlerinin PC performansı yalnızca foton dalga boyuna, foton yoğunluğuna, aydınlatma süresine ve ortamın sıcaklığına değil, aynı zamanda neme de duyarlıdır. Bu sebepten enkapsülasyonun PC özellikleri iyileştirmesi beklenmektedir. Yapılan kaplamalardan sonra enkapsüle edilmiş YHO kaplı camların full spectrum geçirgenliklerine ve uzun süreli optik performanslarına bakılmıştır. Yapılan ölçümler sonucu Al_2O_3 ve SiO_2 'in uzun süreli optik performansı olumlu etkilediği ortaya çıkmıştır. Bunun yanı sıra TiO_2 ile yapılan kaplamanın geçirgenlik değeri diğer metal oksit enkapsülasyonlara göre düşük kaldığı için en kötü performansı TiO_2 sergilemiştir. MOx enkapsülasyon etkisi incelendikten sonra organik kaplamaların etkisi incelenmiştir. Organik malzemeler kullanılarak YHO kaplı camlar üzerine PVB ve PVP polimerleri sol-jel yöntemlerinden olan döndürmeli kaplama yöntemi ile kaplanmıştır. Hızlı, düşük maliyetli, kolay bir yöntem olan sol-jel yöntemi ile PVB ve PVP polimerleri, kaplama hızı ve çözelti konsantrasyonu değiştirilerek YHO cam kaplı filmler üzerine homojen bir şekilde kaplanmıştır. Farklı polimerik çözelti kosantrasyonları ve farklı açısal hızlar kullanılarak kaplamanın yüzeyde en homojen olduğu parametreler optimize edilmiştir. Tezin bu bölümünde metal oksitler ve polimerlerle enkapsüle edilen YHO kaplanarak uzun süreli optik performansları üzerindeki etkileri incelenmiştir. PVB ve PVP enkapsülasyonların uzun süreli optic performanslarına bakıldığı zaman PVB'nin daha uzun süre boyunca yüksek geçirgenlik gösterdiği görülmüştür. Elektron demeti ile buharlaştırma yönteminin avantajı, hassas film kalınlığı sağlanarak, aynı anda (in-situ) pota içinde birden fazla farklı malzeme kaplanabilir. Bu yöntemle MOx aynı kaplama parametreleri ile sentezlenmiştir.

Tezin ilk bölümünde, fiziksel ve kimyasal kaplamalar detaylıca çalışılarak düzgün, kontrollü ince filmler sentezlenmiş ve bu inorganik ve organik malzemelerin PC (pasif cam) özellikler üzerine etkisi kısmen incelenmiştir. Aktif cam olan, akıllı cam olarak da bilinen EC camlarda, perovskit güneş hücrelerinin deşik taşıma tabakasında (HTL) yaygın olarak kullanılan nikel oksit ve tungsten oksit ince filmler kullanılmaktadır. Ticari uygulamalarda çok sık kullanılan manyetik sıçratma yöntemi ile geniş ticarileşme potansiyeli olan bu malzemeler tezin ikinci bölümünde sentezlenmiştir.

Ayrıca, WO_3 ve NiO literatürde yüksek stabilitesi ve dayanıklılığı sebebiyle sıkça kullanılan elektrot malzemeleridir. Bu malzemeler, yukarıdaki belirtilen uygulama alanlarının gerekliğinden dolayı saydam iletken altlıklar (ITO) üzerine manyetik sıçratma yöntemi ile kaplanmıştır. Böylece farklı fiziksel özelliklere sahip altlıklar üzerine farklı kaplama yöntemi ile hem NiO hem de WO_3 başarılı bir şekilde kaplanmıştır. Tezin son aşamasında yakıt hücrelerinde, lityum iyon pillerinde, ince film bataryalarda (TFB), EC aygıtlarda elektrot malzemesi olarak kullanılan LiPON (lithium phosphorus oxy nitrade) katı elektrolit olarak, gümüş elektrotlarının üzerine

manyetik sıçratma yöntemi ile kaplanmış ve karakterizasyonları yapılmıştır. Gümüş elektrotun tercih edilme sebebi katı elektrolitin altında ve üstünde iletken katmanlar oluşturmaktır. LiPON katı elektrolitlerin iyonik iletkenlik değerleri Nyquist diagramı çizilerek hesaplanmış ve literatürle karşılaştırılmıştır. Yapılan hesaplamalar sonucunda elde edilen LiPON iyonik iletkenliği literature oranla daha düşük çıkmıştır.

Özetle, cam altlıklar üzerine NiO, Al_2O_3, SiO_2, TiO_2 ince filmleri elektron demeti buharlaştırma yöntemiyle, PVB, PVP polimerleri sol-jel yöntemi ile kaplanmıştır. ITO kaplı cam altlıklar üzerine, NiO ve WO_3 ince filmler püskürtme yöntemi ile kaplanmıştır. Son aşamada gümüş elektrotlar üzerine LiPON kaplanmıştır. Çok geniş uygulama alanı bulan ince filmler, farklı altlıklar üzerine başarılı bir şekilde kaplanmış ve incelenmiştir.

1. INTRODUCTION

1.1 Overview And Objective

The emphasis of this thesis is to implement different type of thin film coating methods for chromogenic applications. This work mainly focuses on the photochromic and electrochromic multi layer thin films obtained with magnetron sputtering, electron beam deposition and spin coating techniques. The physical and chemical properties of thin films can be controlled and optimized during the coating processes. The long cycle optical performance of the multi layer structure depends on the coating methods and deposition parameters of those layers. For the photochromic thin films, rare earth oxyhydride-based photochromic device is made by encapsulating the photochromic YHO films with different polymers such as, e.g., PVP and PVB deposited by spin coating and with inorganic thin films such as NiO, TiO_2, $Al2O_3$, and SiO_2 deposited by electron beam deposition. For the electrochromic thin films, NiO and WO_3 are coated on top of ITO with magnetron sputtering. A solid electrolyte LiPON is coated with magnetron sputtering. The main objective is to deposit multi layer organic and inorganic films on glass substrates and optimize their deposition parameters for photochromic and electrochromic applications.

1.2 Energy Saving With Chromogenic Materials and Smart Glasses

The word “Chromogenics” is originally comes from the Greek word chromo which means color. Nowadays, it means the field of study of materials that exhibit a change in their color and optical properties as a function of the applied conditions at the environment. Earlier the word chromo was also used in the field of photography for the materials that are sensitive to light like the photographic paper covered with a silver halide emulsion. Unlike photochromism, for this example of photographic paper the color change was irreversible. Hereunder, chromogenics materials show a reversible change in their optical properties in consequence of the application of certain external stimuli like electric field, light, temperature or pressure. After the applied stimulus the

physical properties of the chromogenic material changes in a reversible way. Chromogenic materials are considered as smart materials and they are very useful in energy saving applications (Materials, 2017). One of the widely researched topic at this subject is the smart windows. Smart windows are preferred for modifying the incoming light and solar energy in buildings. It has some other usage areas for some see through applications such as development of visors and windows for the aircraft market that can control glare for pilots and antiglare automotive mirrors or switchable sunroof glazing for automotive industry. It might be also used in eyewear, flat panel displays and advertising screens (Lampert, 2004). In today's world, the global economy requires major changes in energy technology. Because of the increasing population and global warming energy storage devices play a crucial role for the recent studies. For example it is known that, the building sector is responsible for 30%-40% of the primary energy used in the developed countries. Energy saving in buildings plays a crucial role in order to diminish the carbon dioxide content at the atmosphere as it is well known that the atmospheric content of carbon dioxide has grown from~ 315 ppm at the end of the 1950's to ~400 ppm at 2014. The increasing amount of CO_2 is connected with energy generation and is mainly caused by the burning of coal, oil, and gas (Granqvist, 2014). It is known that strict measures should be taken in order to decarbonize the energy sector and increase the energy efficiency by transitioning to renewable energy sources.

As a result, improving the energy efficiency performance of a building is necessary for a sustainable and environmentally friendly society (Long & Ye, 2016). In order to reduce energy in buildings, chromogenic window is a good technologic application. The most studied chromogenic technologies involve thermochromic, gasochromic photochromic and electrochromic windows. Thermochromic materials change their color with increasing temperature. When the temperature of the environment is hot, they reduce their optical transmission and this allows passive solar heating. Thermochromism has been observed in many different compounds; for example, inorganic oxides, liquid crystals, and conjugated oligomers. Vanadium dioxide (VO_2) is one of the most promising thermochromic inorganic oxides (Long & Ye, 2016). Gasochromic materials have an optical reaction to exposure of certain gases. Gaschromism are based on the property of tungsten oxide thin films, which has been

studied mostly, to color in the presence of hydrogen gas with a suitable catalyst (Lampert, 2004). Chemochromic materials are the materials that change color when exposed to specific chemical environment. Electrochromic materials are able to change their optical properties under externally applied electrical voltage or current. With the application of reverse voltage the material turns back to its original transparent state. Some organic and inorganic materials exhibit electrochromic properties through other types of reversible chemical transformations. Among the inorganic compounds, many metal oxides show an efficient form of electrochromic coloration. A number of molecular dyes and conducting polymers are also very efficient electrochromic materials (Materials, 2017). Photochromism is the ability to change color as a response to electromagnetic radiation. The optical properties can be controlled and reversed with the application of light. The color change occurs in the visible and infrared regions. The radiation at this regions causes conductivity and leads to photochromic applications.

1.3 Photochromic Films

Photochromic materials are mostly studied in the last decade so they gained attention from reseachers because of it's importance of reversible color change. PC films respond to light but it cannot be controllled manually so they are considered as passive smart glasses. In the literature, PC materials can be group into two main classes such as organic and inorganic PC glasses. Inorganic PC materials have several sub groups such as alkaline earth sulphies, alkaline earth titanes and rare earth oxyhydrides (Division & Works, 1967).

Yttrium oxyhydride (YHO) is a rare earth oxyhydride which is used as a new inorganic contender that exhibits photochromic properties at room temperature and ambient pressures (You & Karazhanov, 2020)(Baba, Montero, Moldarev, et al., 2020). Also, it belongs to an emerging class of materials called mixed anion systems(Kobayashi et al., 2018)(Kobayashi et al., 2017)(Kageyama et al., 2018) that contain more than one type of anions. YHO is expected to possess exciting properties not exhibited by yttrium oxide or by yttrium hydrides. Distinct from the well-known oxide-based photochromic materials no light induced mid gap states have been reported that would block visible light. Since it is inorganic, durability of the material is expected to be longer than

polymer based PC. Furthermore, YHO possesses greenish color, which is soft to eyes. The transparency of YHO films can be reduced from ~80%-90% in the clear state to ~30%-40% in the photo- darkened state. The photodarkened YHO film thermally bleaches back to its initial yellow clear state at room temperature (You & Karazhanov, 2020). This property provides many opportunities for photochromic applications.

1.3.1 Encapsulation of YHO based photochromic films

Yttrium oxyhydride (YHO) exhibits photochromic properties at room temperature and window treatments are particularly interesting. However, performance of YHO is sensitive not only to photon wavelength, intensity, duration of illumination (Hallaråker, 2018b; J. Montero et al., 2017) and temperature of environment (Hallaråker, 2018a; José Montero et al., 2018), but also on humidity (Baba, Montero, Strugovshchikov, et al., 2020; Moro et al., 2019). On the other hand, prolonged illumination of YHO with UV light did not change the concentration of the oxide and hydride anions inside through the sample thickness (Granqvist, 2014; Moldarev et al., 2020; Vyas, 2019), it was demonstrated that the photochromic effect in YHO is a bulk effect (Moro et al., 2019). So, it if the photochromism is bulk effect, it is unclear why it depends on presence of humidity in the film. To resolve these challenges, it is crucial to study role of encapsulation layers on photochromic properties of YHO.

2. THIN FILM DEPOSITION FOR PHOTOCHROMIC APPLICATION

Thin film production is considered to have a very high impact on advanced technology such as telecommunications devices, environmental applications, optical devices, and energy storage devices. The application area highly depends on the crystal structure, morphology and stability of the thin films. These properties depend on deposition techniques. Thin films can be deposited by vacuum and solution based coating techniques. Vacuum based deposition techniques are subdivided into chemical vapor deposition (CVD) and physical vapor deposition (PVD) techniques. The deposition techniques are given in Figure 2.1 (Vyas, 2019)

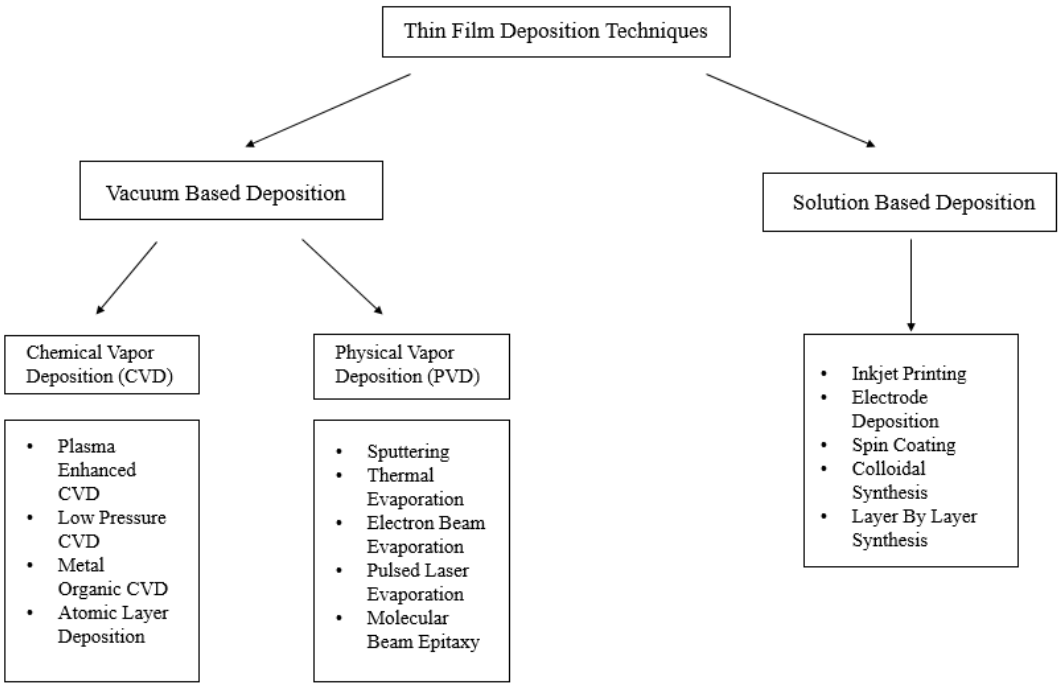


Figure 2.1 Classification of thin film deposition techniques

One of the common used vacuum based deposition technique is CVD. The synthesis process occurs when the chemical compounds react in their vapor phase on to a heated substrate to form a solid deposit (Pierson, 1999). The CVD technology connects several scientific and engineering subjects such as plasma physics, thermodynamics,

fluid dynamics, kinetics and of chemistry (Pierson, 1999). The mentioned reactions can be activated by several methods. Chemical Vapor Deposition can be divided such as plasma enhanced CVD, low pressure CVD and metal organic CVD. When compared to other methods, CVD operations are simple so they could be optimized experimentally by changing the reaction chemistry, or the deposition variables until a coating of choice is attained. For some cases, it is still the most efficient way to proceed. Plasma enhanced CVD, includes a new remote inductively coupled RF plasma source which minimizes the orientational effect during the catalyst-free growth. Recently this technique is preferred for synthesis of graphene nanosheets (Cuxart et al., 2017). Metal Organic CVD (MOCVD) is a CVD technique at which organo-metallic precursors. Precursors are transported to the substrate by the carrier gas (argon) and adsorbed on the substrate surface (Niu et al., 2013). Atomic layer deposition (ALD) is a very important vapor deposition technique for industry and research. ALD is a technique for growing thin films. The desired materials are formed via chemical surface reactions. Gaseous precursors are introduced into the reaction chamber to the substrate surface. Due to its atomic level control and uniformity ALD is used especially in the microelectronics industry (Leskelä et al., 2014). Other vacuum based deposition technique is called Physical Vapor Deposition. This technique is divided into six subgroups which are electron beam evaporation, pulsed laser evaporation, thermal evaporation, magnetron sputtering, molecular beam epitaxy and atomic layer deposition. Thermal evaporation is a widely used method for producing coating a thin layer. The source material is evaporated under vacuum (below 10^{-4} Pa) due to high temperature (Bashir et al., 2020). The vapor particles move towards the substrate and they change into their solid state on to the substrate. The high melting points are necessary for metals is reached via exposure of direct current (DC). Pulsed Laser Deposition (PLD) is a category of PVD. The desired material is vaporized with a high power density and a narrow frequency bandwidth laser is used as a laser source. This deposition technique is used for synthesizing nanotubes, nanopowders, and quantum dots (Siva Prasanna et al., 2018). Molecular Beam Epitaxy (MBE) allows the epitaxial films to grow while well-defined thermal beams of atoms react at a crystalline surface. This technique is used for mainly synthesizing semiconductors as well as metals and insulators metal oxide nanoparticles (Siva Prasanna et al., 2018).

Solution based coating methods have many compelling properties such as reduced cost, improved performance and functionality. Inkjet printing utilizes a stable laminar liquid jet and the jet is scanned continuously across the substrate. There are previously defined wetting and nonwetting areas. The ink spreads on the substrate due to previously formed containment pattern (Chesterfield et al., 2011). Pulse Electrode Deposition (PES) is a technique modifies metal surface by using high current electrical pulses of short duration. The high current melts the electrode and the material is deposited on the substrate. Hence, the electrode material should be conductive. PES has a unique role because the process allows deposition of ultra-hard, corrosion- and erosion-resistant ceramic coatings on metals (Agarwal & Dahotre, 1998). Colloidal method uses organic solvents which form stable colloidal suspensions to produce thin film coatings. Since colloidal synthesis is a hot-injection and heating-up technique since it is very rapid, versatile, reproducible, easy to control, and relatively safe because the reaction occurs under atmospheric pressure and at lower temperature than other techniques (Zheng & Xu, 2014). Layer by layer (LbL) method is developed for depositing oppositely charged materials in an alternating way. The layers can be deposited in different coating techniques such as spin coating, spray coating or dip coating. By LbL technique various materials like nanoparticles, ceramics, metals and even biological molecules. At this thesis, mainly used deposition techniques are magnetron sputtering, electron beam deposition and spin coating techniques. The detailed information about this techniques will be given at the upcoming related chapters.

2.1 Electron beam deposition of inorganic oxides films

Electron beam (e-beam) deposition is a lithography technique containing volatile precursors which dissociates by using a focused ion beam in low vacuum environment to create uniform thin films. During evaporation process, the current passing from a tungsten filament creates heat and it leads to an electron emission. After the electron emission, with the applied high voltage between the tungsten filaments the liberated electrons are accelerated. Inside the apparatus there is a strong magnetic field that directs the liberated electrons inside a unified beam. Electron hits the surface of the deposition material, the energy of the electron passes to the deposition material and

this causes evaporation and deposition on the substrate. There is an option of adding a partial pressure of reactive gas, such as oxygen, argon, nitrogen to the chamber during evaporation can be used to reactively deposit non-metallic films. This technique is used for many applications including metallization, dielectric coating and optical coatings. Electron beam deposition has many advantages when compared with other deposition technologies.. Additionality, it can eliminate the unwanted contamination because it can better maintain the purity of the deposited metal. This promotes very high deposition rates and evaporation of high temperature materials and refractory metals (*Electron Beam Evaporation | Angstrom Engineering*, n.d.)

3. EXPERIMENTAL PROCEDURE

YHO thin films were prepared by our reseach group onto glass substrates which are microscope slides (76×26mm and 1mm thick) by magnetron sputtering in a Leybold Optics A550V7 sputter unit. After the film growth the substrate is kept under glow box to prevent excess oxidization. Encapsulating the YHO films with various metal oxide thin films were coated by e-beam deposition technique because of purity of the deposited metal, high deposition rates and numerious advantages in this thesis. The thin film growth was made with Angstrom Engineering Deposition tool. During this process, current is passed through a tungsten filaments and it leads to electron emission. With a strong magnetic field, accelerated electrons are transferred towards the crucible containing the material to be deposited. When the electrons hit the surface of the crucible, it causes the material to evaporate. The sublimation happens onto the substrate and the deposition process finishes. In this work, during the e-beam process the purpose was to obtain films which were non-metallic because otherwise the photochromic property and performance of encapsulated YHO films could not be observed by trial and error. Adding partial pressure of a reactive gas such as oxygen inside the chamber plays a key role in order to obtain transparent, non-metallic films. Evaporation rate is optimized according to required oxygen level. E-beam evaporation has many advantages for obtaining uniform films all over the substrate surface because the e-beam source is capable of heating materials to much higher temperatures by using a crucible heater. E-beam deposited films can also better maintain purity because the crucible tightly confines the electron beam heating to only the area occupied by the source material, eliminating any unwanted contamination from neighboring components. Inside of the chamber is shown in Figure 3.1.

Figure 3.1 The chamber of e-beam deposition tool.

The substrate holder rotates on the upper wall of the chamber and it holds up to five substrates each time. The samples are attached to the surface of the holder with screws as it can be seen in Figure 3.2

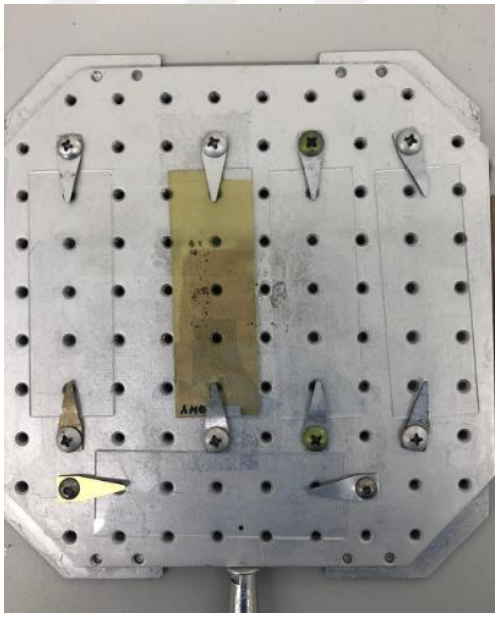


Figure 3.2 Substrate holder for each deposition (YHO coated glass and only glass attached to the sample holder).

Inside the system there are multiple crucibles containing nickel, silicon oxide, titanium and aluminum as shown in Figure 3.1. For these metals, many trials were made for

obtaining non-metallic, oxygenized and transparent films. During the deposition base pressure is kept under $2x10^{-6}$ Torr. The deposition pressure was different for each metal but they were all around 10^{-5} Torr. Oxygen flow is fixed to 10 sccm and it is the only gas used inside the chamber. Encapsulation thickness is 100 nm and the rate is kept 0.5 A/s. Power was given as percentages and during deposition each metal's power was between 15%-25%. After applying these parameters, the obtained films were in accordance with the desired physical properties. The photochromic property of the double layer films are investigated by illuminating one side of the encapsulated YHO with a UV lamp. One side is kept without illumination by the help of a dark paper. The dark paper covers half of the coated glass to see the optical contrast between the illuminated and non-illuminated part.

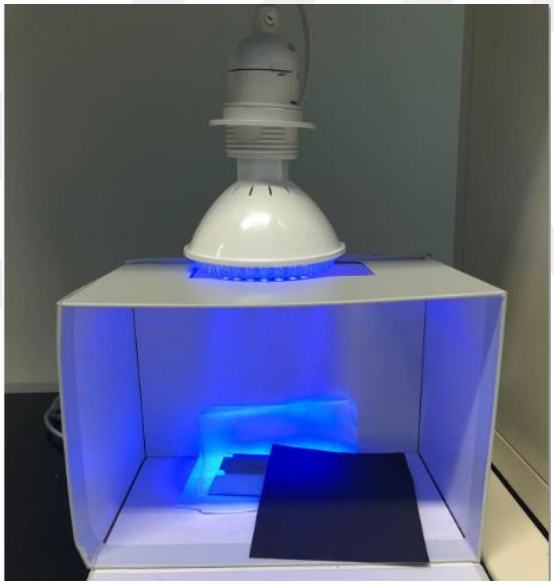


Figure 3.3 UV illumination set-up.

The initial stage of the encapsulated YHO films are yellow and transparent. Under ambient conditions with illumination the photochromic films become darker after couple of minutes. All samples are illuminated with a LED lamp. The LED lamp has a wavelength~400 nm and the intensity~10 mW/cm^2. Before doing the cyclic testing, the films were saved inside the glove box to minimize the contamination.

3.1 NiO

At this study, the effect of various metal oxide encapsulation on top of YHO films and their optical properties are discussed. All of the metal oxides were grown by e-beam evaporation technique. During the evaporation the chamber is always under Ar atmosphere. The YHO on glass substrate was kept at room temperature at each try. Metal oxide coatings were first coated on glass substrates to optimize their transparency. After that they were all coated on glass/YHO substrate to investigate the photochromic effect. The objective is to prepare double layer photochromic films and create new photochromic device design. In the literature, it has been detected that NiO is considered as almost transparent, wide band gap semiconductor and it has p-type semiconductor behavior (Patel et al., 2011). NiO thin films behave p-type semiconductor due to holes generated by Ni vacancies in the lattice. The stoichiometric NiO exhibits a resistivity but it can be lowered by oxidizing Ni^{+2} ions to Ni $^{3+}$ ions resulting from an appearance of nickel vacancy or interstitial oxygen in NiO crystallites (Sato et al., 1993). It also has a very good chemical stability therefore NiO is an interesting candidate for materials applications (Fasaki et al., 2010). NiO is a semiconductor with the band gap energy of 3.5 eV. It is a good transparent semiconductor because of the wide band gap. In the literature the reported band gap of the NiO films is in the range of 3.1 ~ 4.3 eV at 300 K, which depends on deposition parameters such as the substrate at room temperature by DC sputtering at an thickness of the film (Shin et al., 2013). The darkening and bleaching of NiO encapsulated YHO is shown in Figure 3.4. The thickness of NiO coated layer is 100 nm.

(a) (b) (c)

Figure 3.4 NiO encapsulated YHO films (a) As-deposited film (b) UV illumination film (c) bleached film.

Before this trial the rate was higher and the arranged thickness was 200 nm, 150 nm, and 100 nm. Even though the thickness was decreased the coating was still metallic. In order to solve this problem, the deposition rate was decreased from 2 Å /s to 1.5 Å /s and then 1 Å /s to 0.5 Å /s. The best non-metallic and transparent result was with 0.5 Å /s. If this process of obtaining a non-metallic coating did not work another plan was to heat the substrate to avoid the metallic effect but it was not applied because after decreasing the rate the transparency was sufficient to see the photochromic behaviour of YHO. The photochromic effect was checked with a UV lamp with the wavelength of 405 nm. The refractive index of NiO is 2.1818 (Ukoba et al., 2018). It is found that for in situ oxidized NiO the work function can be as high as 6.4 eV but after adsorption of residual gases in vacuum the work function decreases between 5.2 and 5.6 eV. Ex situ and air exposed NiO has a lower work function due to hydroxylation of the oxide surface (Greiner et al., 2010). Therefore, NiO is selected for the first metal oxide encapsulation. The optimization process was very important to obtain transparent and uniform encapsulation. Apart from the literature search, there were many trails to get the oxygenized and non-metallic coating. The power parameter of the e-beam device used in this part of the thesis has been pre-calibrated. After this calibration, the power values read on the device are in percentage. The percent power values were kept between 10% and 20% in order to continue successfully without stopping throughout the metal oxide coating process.The summary of deposition parameters of NiO used are given in Table 3.1.

Table 3.1 E-beam deposition parameters for optimizing NiO encapsulation.

Base Pressure (Pa)	Deposition Pressure (Pa)	Rate (Å /s)	Oxygen flow (sccm)	Thickness (nm)
$8.0x10^{-4}$	$2.6x10^{-3}$	1.5	0	200
$3.3x10^{-4}$	$9.0x10^{-3}$	1.0	5.0	150
$7.6x10^{-4}$	$9.3x10^{-2}$	1.0	10.0	200
$2.6x10^{-4}$	**$11.9x10^{-3}$**	**0.5**	**10.0**	**150**

Herein, NiO coating is prepared on unheated substrate by using Ni pellets under argon and oxygen atmosphere. Film thickness was measured by the thickness monitor of the e-beam deposition.The last line of Table 3.1 was the most suitable coating parameter to detect the photochromic behavior of YHO. The other lines were not transparent

enough to see the reversible color change. In the fist trial the oxygen pressure was zero sccm and the encapsulation had a reflection like a mirror so in order to have more transparent encapsulation the oxygen flow was increased. As a result, the optical and electrical properties of nickel oxide can be altered easily for the desired purpose.

3.2 SiO_2

Like NiO encapsulation non-metallic layer, SiO_2 films were used for the same purpose. SiO_2 films were later prepared by evaporating SiO_2 pellets under oxygen partial pressure. The substrate was at room temperature during the process. At previous works it is discussed that only the films prepared by evaporating SiO_2 in an oxygen atmosphere are photoluminescent at room temperature (S. Zhang et al., 1998). Crystalline silicon is a well-known and used material in the microelectronic research. SiO_2 is considered as an indirect gap semiconductor so light emission in the visible is inefficient but it has a strong visible photoluminescence from porous silicon at room temperature (Sasaki & Ehara, 2013). The refractive index of SiO_2 samples were investigated and it is seen that the oxygen content at the chemical formula has a direct effect on the refractive index. According to previous works, when the oxygen content increases inside the SiO_2 chemical structure the refractive index decreases. Oxygen content between 0 and 2 are investigated and the refractive index varies between 1.5 and 3.3. The band gap of SiO_2 increases as a function of the oxygen content. Oxygen content between 0 and 1.6 are investigated and the band gap increases with the increasing oxygen. The band gap varies between 1.5 and 3.5 eV (Tomozeiu, 2005). SiO_2 is selected to be the one of the encapsulation materials since the properties of YHO are not blocked. The trials of deposition was made under the conditions shown at Table 3.2.

Table 3.2 E-beam deposition parameters for optimizing SiO_2 encapsulation.

Base Pressure (Pa)	Deposition Pressure (Pa)	Rate (Å /s)	Oxygen flow(sccm)	Thickness (nm)
$2.5x10^{-4}$	$2.6x10^{-3}$	1.5	0	100
$4.5x10^{-4}$	$7.8x10^{-3}$	1.0	5.0	100
$2.6x10^{-4}$	$4.0x10^{-3}$	1.0	10.0	100
$2.6x10^{-4}$	**$10.1x10^{-3}$**	**0.5**	**12.0**	**100**

By using this conditions, SiO_2 film was transparent and uniform. The oxygen partial pressure is very critical for this experiment because higher oxygen partial pressure leads to smaller Si crystallite and higher oxygen concentration in the film. This has a direct relation with the optical properties of the YHO encapsulated with SiO_2 films (S. Zhang et al., 1998). The illumination and darkening stages demonstrates that the transparency of the deposition was suitable to see the photochromic behavior of YHO. shown in Figure 3.5.

(a) (b) (c)

Figure 3.5 SiO_2 encapsulated YHO films (a) As-deposited film (b) UV illumination film (c) bleached film.

As it can be seen in Figure 3.5, SiO_2 was successfully deposited on YHO as a transparent and uniform layer when the oxygen increased to 12 sccm and the deposition rate decreased to 0.5 Å /s

3.3 TiO_2

Another encapsulation was made with titanium oxide. TiO_2 thin films are frequently preferred for optical coatings because transparent in the visible and near infrared

ranges. Due to its high refractive index it is a good candidate for photochromic applications. It also has good mechanical properties and chemical resistance (Yao et al., 2009). TiO_2 has four forms that are amorphous, anatase and rutile, brookite. Anatase state shows crystallization at approximately 300°C and rutile phase crystallizes at 1100°C. Rutile is the most thermodynamically stable phase and has the highest refractive index n_{rut}=2.9 and refractive index of the anatase phase is n_{ana}=2.49. There ha not any report of depositing rutile film by electron beam (Yao et al., 2009). The deposition was made under room temperature so it is thought that the film is amorphous. In metal oxide encapsulation trials, TiO_2 was the metal oxide film where transparency is the hardest to achieve. Just like the other metal oxides plenty of experiments were made and the optimization process of TiO_2 is given in Table 3.3.

Table 3.3 E-beam deposition parameters for optimizing TiO_2 encapsulation.

Base Pressure (Pa)	Deposition Pressure (Pa)	Rate (Å /s)	Oxygen flow(sccm)	Thickness (nm)
$4.0x10^{-4}$	$10.7x10^{-5}$	1.0	0	100
$6.4x10^{-4}$	$3.9x10^{-5}$	1.0	5.0	100
$2.4x10^{-4}$	$2.6x10^{-5}$	1.5	10.0	100
$2.6x10^{-4}$	**$1.6x10^{-5}$**	**0.5**	**10.0**	**100**

After the deposition process it is observed that TiO_2 films were darker than other metal oxides even before UV illumination. In other words, the transmittance of TiO_2 encapsulated YHO was the lowest compared to other metal oxide encapsulations. This situation made the optimization process even harder. The oxygen flow is increased to 10 sccm and the depositon rate was decreased to 0.5 Å /s. At that condition (which is the last line of the table) the encapsulation had a dark navy blue color that prevented us from seeing the reversible color change with the UV illumination. The illumination and the darkening was less visible and it is given in Figure 3.6. Further research should be undertaken to reach titanuım oxide film with higher transparency

(a) (b) (c)

Figure 3.6 TiO_2 encapsulated YHO films (a) As-deposited film (b) UV illumination film (c) bleached film.

The reversible color change is seen after many trials but our aim was to make the metal oxide encapsulation as transparent as possible and this film turned out to be darker than expected. We can deduce that the transmission will decrease even when looking with the naked eye.

3.4 Al_2O_3

Lastly, Al_2O_3 film was selected due to their high dielectric strength, high transparency down to 250 nm and durability against hostile environments. The common application areas of Al_2O_3 are microelectronic devices and sensors as well as refractory coatings, antireflection coatings and anticorrosive coatings (Shamala et al., 2004).

The refractive index of Al_2O_3 films with various thicknesses from 50 nm to 200 nm are investigated and it is found that electron beam deposited Al_2O_3 films have the highest refractive index (1.61-1.63) (Puri, 1996). Film prepared by electron beam evaporation technique at ambient substrate temperature has an optical band gap of 5.75 eV (Shamala et al., 2004). Optical properties and stability of Al_2O_3 film depend not only on the deposition technique but also on deposition conditions. The summary of the optimized deposition parameters are given in Table 3.4**.**

Table 3.4 E-beam deposition parameters for optimizing Al_2O_3 encapsulation.

Base Pressure (Pa)	Deposition Pressure (Pa)	Rate (Å /s)	Oxygen flow(sccm)	Thickness (nm)
$2.6x10^{-5}$	$6.6x10^{-4}$	1.0	0	150
$6.6x10^{-5}$	$10.6x10^{-4}$	1.0	5.0	100
$5.0x10^{-5}$	$6.1x10^{-4}$	1.5	10.0	100
$2.5x10^{-5}$	**$8.0x10^{-4}$**	**0.5**	**10.0**	**100**

In this case, the last line of the table shows the parameters that are transparent enough to be subjected to UV testing. The illumination and darkening processes are given at Figure 3.7.

(a) (b) (c)

Figure 3.7 Al_2O_3 encapsulated YHO films (a) As-deposited film (b) UV illumination film (c) bleached film.

After the UV test, the reversible color change of YHO can be easily seen with the naked eye. This proves that Al_2O_3 encapsulation parameters were suitable.

All of the mentioned metal oxides are coated because although yttrium oxyhydride exhibits photochromic properties at room temperatures and ambient pressures, encapsulating YHO with metal oxides have a positive impact on the long cycle photochromic performance of YHO. Photochromic performance of YHO is sensitive to humidity which is proved to be affecting the bleaching performance of YHO films.Encapsulating YHO is one of the approach solving the mentioned issue.

To sum up, metal oxide encapsulation experimental sets were successfully coated and their long cycle optical measurements will be given at photochromic measurement section. After optimizing metal oxides, polymer encapsulations are made to detect whether the optical performance can be improved like metal oxide encapsulations.

3.5 Wet coating of organic synthetic biocompatible films: PVB, PVP

Recently, the interest in organic semiconductors has increased as a result of their potential use in new electronics applications such as radio frequency identification tags, biosensors, or photovoltaics. The development of solution processable organic

semiconductors made spin coating a favorable method due to its low-cost and speed (Delongchamp et al., 2005). Spin-coating is used in applications such as coating of photoresist on silicon wafers, sensors, protective coatings, paint coatings, optical coatings and membranes (Norrman et al., 2005). Spin coating is a deposition technique which produce thin films from polymers. Spin coating is a solution based process which allows a low-cost deposition. Organic materials can be deposited uniformly on flat surfaces by centrifugal force. There is a continuous rotation until the polymeric solution is dispensed onto the substrate. The desired thickness varies according to spin speed and the viscosity of the solution. The polymeric solvent is volatile so it evaporates during deposition. Spin coating has four stages(Yilbas et al., 2019):

- Deposition
- Spin up
- Spin off
- Evaporation

At the first stage the material is deposited on the substrate and the solvent evaporates during the spin up and spin off process. High spinning speed causes thinning of the deposited layer. This stage is followed by drying of the applied layer. A simple proportion is made related to the speed of the spin to estimate the film thickness. The thickness is inversely proportional to the square root of angular velocity.

However, this rule does not always apply and does not allow for predictions of film thickness without experimental data (Emslie et al., 1958) The experiments are made with spin coating set up which is shown in Figure 3.8.

Figure 3.8 Spin coating set-up.

The planer substrate holder allows deposition of uniform thin films. Spin coating is described as the process of applying a solution to a horizontal rotating disc, resulting in ejection and evaporation of the solvent and leaving a liquid or solid film.

In our case, dynamic spin coating is used for PVP and PVB encapsulation on top of YHO coated glass. The substrate is rotated in different speeds in order to obtain the most uniform films. The concentration of the polymeric solution is also important because it has an effect on the spreading. To this respect, for PVB and PVP 1%, 5% and 10% of polymeric solution is prepared by using ethanol as a solvent. The powder polymers were added to 1 ml containing ethanol and mixed with a magnetic stirrer. All of the percentages were soluble by 1 ml ethanol. After that, 100 micro liter of the solution is applied on the center of the YHO coated glass. After many trials the best spreading was observed at 2000 rpm rotational speed. Before deciding that, 500, 1000 and 3000 rpm rotational speeds were tried but the spreading was optimal at 2000 rpm. The selected concentration for the cycle testing was 10% for both PVB and PVP. The encapsulated films were kept inside the glow box to prevent any contamination.

3.5.1 PVB

The chemical structure of PVB should be mentioned before talking about the spin coating conditions. Polyvinyl butyral (PVB) is formed from the reaction of an alcohol and aldehyde. PVB is generally made as a mixture of PVB, polyvinyl alcohol (PVOH), and polyvinyl acetate segments. The relative amounts of the segments depend according to the random distribution of the molecular chain. The representation of the structure of PVB is given in Figure 3.9**.**

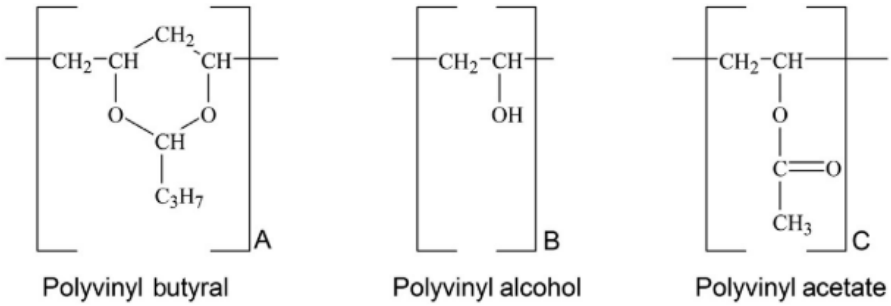


Figure 3.9 Structure of polyvinyl butyral (PVB)**.**

PVB is described as a biocompatible and non-toxic polymer (McKeen, 2017). It has good solubility in alcohol so it is solved in ethanol for electrospinning. Most common application areas are adhesive interlayer in safety glass, wound dressing, and coating film (Chen et al., 2019). Dynamic spin coating is used for PVP (poly (4-vinylphenol)) and PVB (poly (vinyl butyral)) encapsulation on top of YHO coated glass. Several experiments were made. For example, the substrate was rotated in different speeds in order to obtain the most uniform films. The trial conditions of the polymeric solution (PVB) is summarized in Table 3.5.

Table 3.5. Spin coating solution parameters for PVB.

Solution Percentage (%)	Amount of PVB powder (mg)
1.0	26.025
5.0	126.99
10.0	233.59

After depositon, the yelow color of YHO can still be seen because as deposited polymeric encapsulation is transparent. The PVB and PVP encapsulated YHO films after the encapsulation are shown in Figure 3.10.

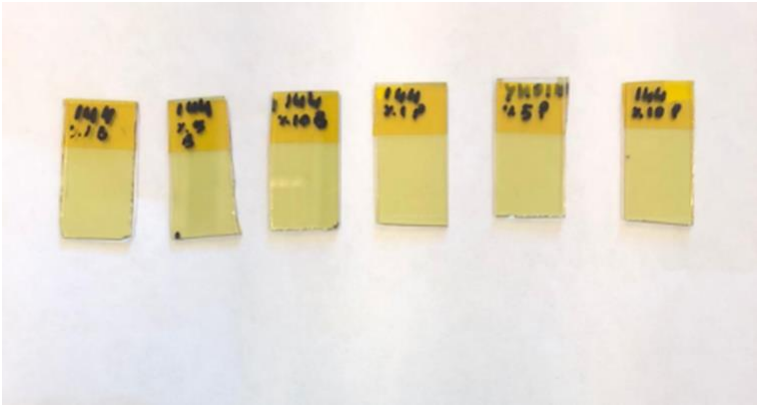


Figure 3.10 PVB and PVP encapsulated YHO films.

In Figure 3.10 both PVB and PVP solutions are tried with the percentages mentioned in the Table 3.5 above. The polymeric solution is spread by the centrifugal force. The concentration of the polymeric solution is also important because it has an effect on the spreading. To this respect, for PVB and PVP 1%, 5% and 10% of polymeric solution is prepared by using ethanol as a solvent. The powder polymers were added to 1 ml containing ethanol and mixed with a magnetic stirrer. All of the percentages were soluble by 1 ml ethanol. After that, 100 micro liter of the solution is applied on the center of the YHO coated glass. After many trials the best spreading was observed at 2000 rpm rotational speed. The polymer encapsulated YHO films were dried on top of the hot plate at 100 °C for 15 minutes. The encapsulated films were kept inside the glow box to prevent any contamination.

3.5.2 PVP

Polyvinylpyrrolidone (PVP) is shortly called polyvidone or povidone. PVP is prepared by free-radical polymerization from the monomer N-vinylpyrrolidone in the presence of AIBN as an initiator.The polymer synthesis process is shown in Figure 3.11.

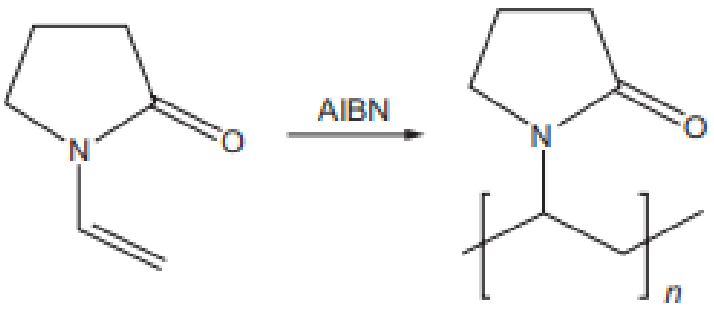


Figure 3.11 Synthesis of polyvinylpyrrolidone.

Before polymerization the powder form of PVP is very light. The polymeric solution is obtained after adding ethanol. PVP is used as a binder in many pharmaceutical tablets. PVP added to iodine forms a complex called povidone-iodine that possesses disinfectant properties (Kariduraganavar et al., 2014). PVP is selected as the second polymer because is a good candidate due to excellent wetting properties. To be able to maximize the adhesion to the surface the deposition conditions should be optimized.The deposition paremeters of PVP are given in Table 3.6.

Table 3.6 Spin coating solution parameters for PVP.

Solution Percentage (%)	Amount of PVB powder (mg)
1.0	26.662
5.0	133.685
10.0	269.04

After the deposition is made, the same procedure was followed for PVP. Like the previous PVB coating, the best coverage was detected at 10% of concentration at 2000 rotational speed.

3.6 Photochromic Thin Film Measurements

Ultraviolet-visible (UV-vis) spectroscopy is used in quantitative analysis which measures the amount of photons (the intensity of light) absorbed after it passes through sample. Spectrophotometer uses two different range of wavelength. The ultraviolet

range is between 185-400 nm and the visible range is between 400-700 nm of electromagnetic radiation spectrum (Zwinkels, 2020). The mentioned optical spectrum is given at Figure 3.12 down below:

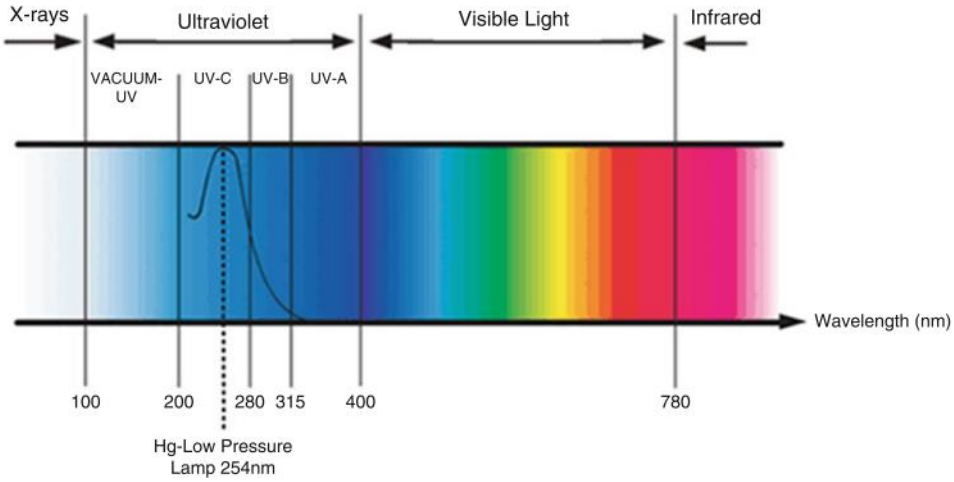


Figure 3.12 The regions of the electromagnetic spectrum.

As it can be seen above, only the frequencies between 10^{14} to 10^{15} s^{-1} is the visible light portion of the spectrum. This means that visual receptors in the human eye can only be stimulated with visible region of the optical spectrum. Before long cycle illumination and darkening, the transmittance of YHO coated glass and encapsulated YHO (with metal oxides and polymers) are measured to detect and compare the optical property of each case with only YHO coated glass. This measurements are made because at the beginning the encapsulation materials (metal oxides and polymers) should not have a considerable influence on the transmission of YHO. Otherwise it would be difficult to detect the optical contrast of encapsulated films under UV light. Optical transmittance (T) is measured for as deposited YHO film and encapsulated YHO films (polymer and metal oxide encapsulations). The YHO films are known to darken reversibly under UV light. At this part, the optical transmittance before and after encapsulation is shown. They are all measured with a Perkin Elmer Lambda 35 UV/VIS Spectrometer in a scanning mode with probing light between [190−1100] nm. The optical transmittance of the encapsulated films are given in Figure 3.13.

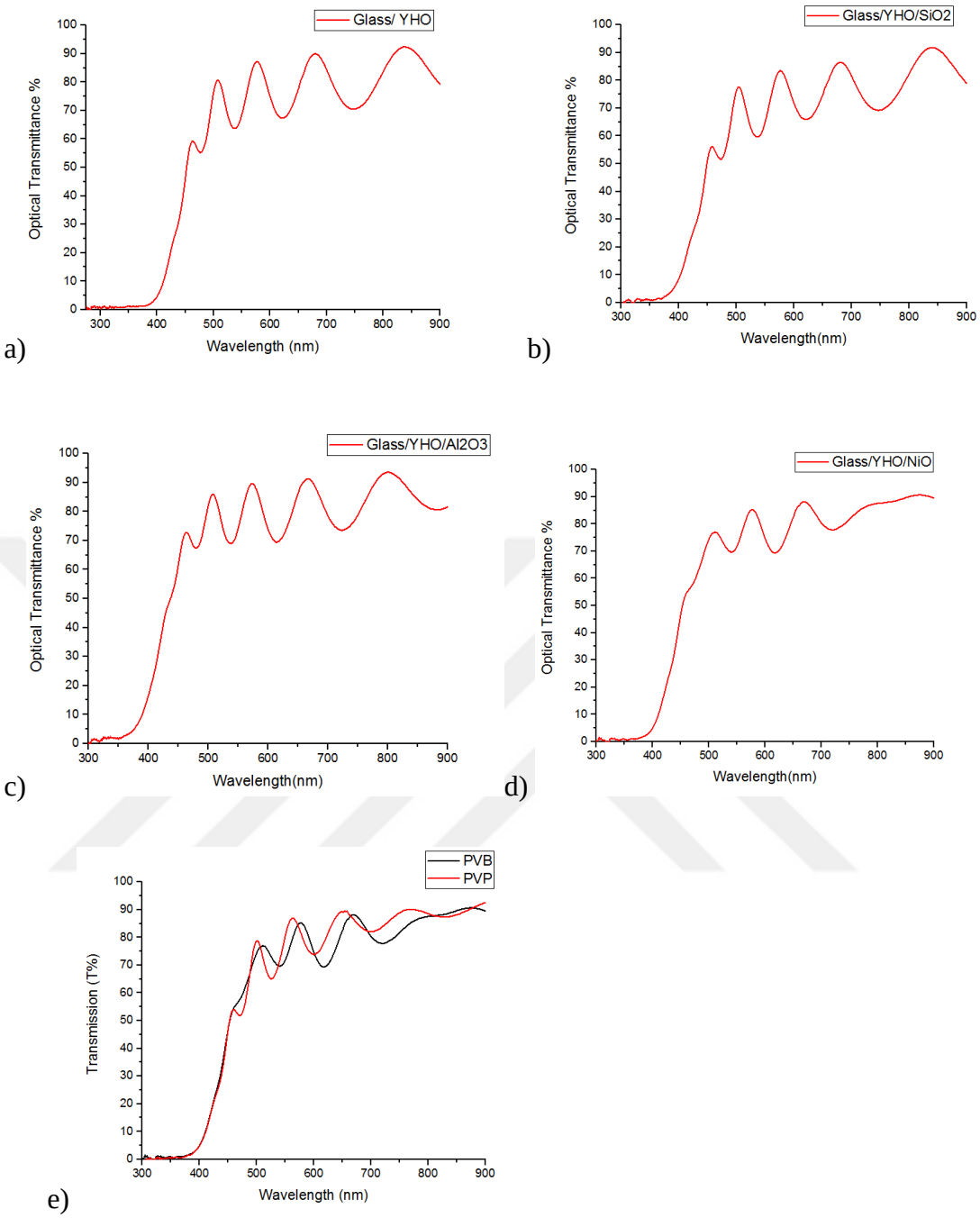


Figure 3.13 Transmittance (T %) vs. wavelength (nm) graphs of a) only YHO coating b) SiO_2 encapsulated YHO c) Al_2O_3 encapsulated YHO d) NiO encapsulated YHO e) PVB and PVP encapsulated YHO.

In these graphs, for all the encapsulated photochromic samples, the transmission did not drastically changed (according to only YHO coated glass). The comparison of optical transmittance is given in Figure 3.14.

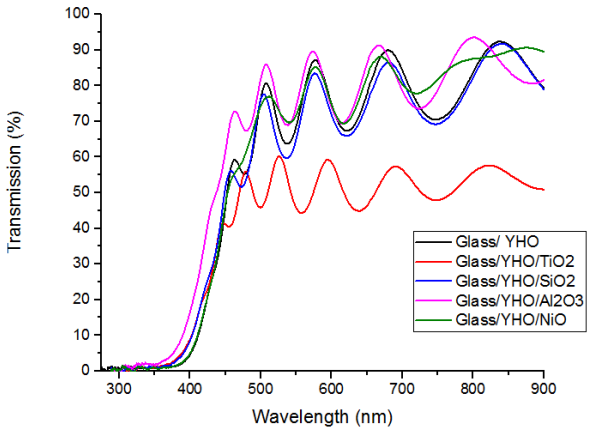


Figure 3.14 Transmission (%) vs. wavelength (nm) comparison of only YHO coating and metal encapsulated YHO.

When the transmissions are compared between only YHO coated and metal oxide encapsulated YHO, the transmission of Al_2O_3 encapsulated YHO is higher than only YHO coated glass. NiO encapsulated YHO and SiO_2 encapsulated YHO has very close transmission to only YHO coated glass. TiO_2 shows the lowest transmission. This was expected after the experimental process because even before the illumination the color of the encapsulation was dark blue while other oxides were very transparent.

After that, the long term photochromic transition of each case is investigated by cyclic testing. Average transmittance measured between 600 and 900 nm during 0.5 h illumination followed by 1 h darkness in a sample. The illumination and darkening is shown in Figure 3.15.

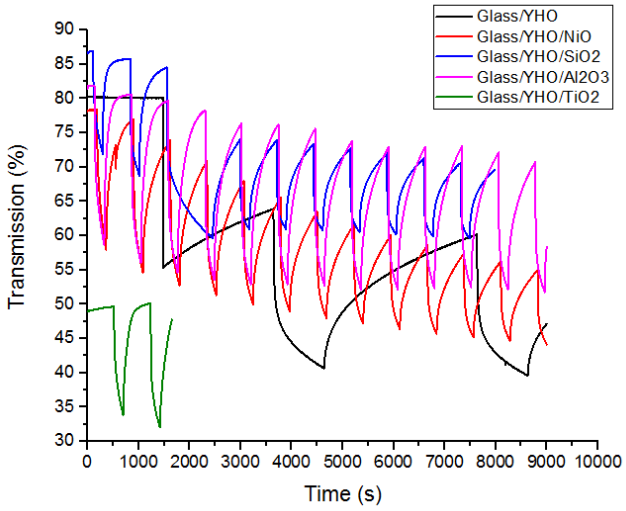


Figure 3.15 Cycle testing of metal encapsulated YHO films.

Figure 3.15 shows that encapsulations with Al_2O_3 and SiO_2 have increased the long-term optical durability of YHO coating. This proves that long cycle transmission performance can be improved by encapsulating YHO. After this result, it should be investigated whether this behavior can occur in other materials as well. Herein, the following graph (Figure 3.16) shows the comparison long time optical performance of PVB and PVP coated YHO.

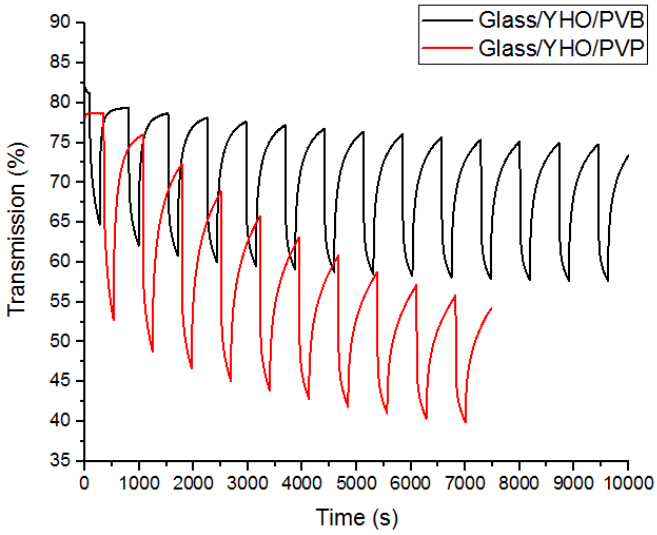


Figure 3.16 Cycle testing of polymer encapsulated YHO films.

From this graph, it is detected that the long cycle transmission performance of PVB encapsulated YHO is better than PVP encapsulated YHO. It is found experimentally that PVB increase the optical performance of YHO photochromic films in terms of long cycle testing.

3.7 Thin Film Deposition For Electrochromic Application

3.7.1 Magnetron Sputtering of inorganic oxide films

Magnetron sputtering is considered as a physical vapor deposition technique widely used to produce thin films. The main components of this technique is substrate holder, target, power supplier, vacuum pump and working gas. The target material is deposited on to the substrate via ion bombarding. The atoms of the target material are ejected in the direction of a substrate. Inside the vacuum chamber there is an inert gas which is mostly Ar and the gas is ionized and forms a plasma. There is a permanent magnet behind the target where the strength of the magnetic field is adjusted so that the electrons follow a cycloidal motion in front of the target, confining the plasma and increasing the ionization efficiency, whereas the motion of the heavier ions remain unaffected (Olsen, n.d.). Ar ions inside the vacuum chamber are positively charged (Ar^+) and they are accelerated onto the surface of the target. Because of this motion multiple collisions happen with the atoms within the top layers of the target. If the energy of the incoming ions are too high, the ions are implanted into the target, but if the energy is too low, the ions are reflected off or they are adsorbed onto the surface. The energy of the ions are adjusted via the applied voltage. The number of the ejected ions and the deposition rate are proportional to the discharge current. Magnetron sputtering is a high-rate vacuum coating technique for depositing metallic or alloy thin films onto a range of materials with thicknesses up to 5μm (Safavi et al., 2020). It has important advantages over other vacuum coating techniques which allows a large number of commercial applications such as microelectronic fabrications. Some of the most mentioned advantages are:

• High deposition rate
• The ability to use metal and alloy targets
• High purity films

• Ability to coat heat-sensitive substrates

• Excellent uniformity on large-area substrates(Tudose et al., 2019)

After ion bombardment, another important process is the emission of secondary electrons from the target surface. The secondary electrons are released as a result of the incident ions interaction with the target. These secondary electrons allows the glow discharge to stay present. The sputter process has almost no restrictions in terms of the target materials. It can be pure metals where a DC power is preferred. For semiconductors and isolators RF power or pulsed DC can be preferred. Deposition can be carried out in inert gas only (non-reactive) or with reactive gas discharges with single or multi elemental targets. The magnetron sputtering set-up which is used at this part of the thesis is shown in Figure 3.17.

Figure 3.17 Moorfield - DC/RF Magnetron sputtering set-up.

WO_3, NiO and LiPON is produced with magnetron sputtering technique. The details will be discussed in the next sections.

3.7.2 WO_3

Tungsten oxide (WO_3) is an electrochromic material widely used for smart windows, electrochromic devices, automotive rear-view mirrors, gas sensors, and organic/inorganic hybrid memory devices (Subrahmanyam & Karuppasamy, 2007). WO_3 was deposited onto ITO (indium tin oxide) coated glass. Generally, some of the most commonly employed deposition techniques are thermal evaporation, electron beam evaporation, sputtering, pulsed laser ablation, chemical vapor deposition, sol–gel coating, and electrodeposition(Subrahmanyam & Karuppasamy, 2007). Tungsten oxide thin films are prepared with tungsten metal with oxygen gas by using direct current (DC) magnetron sputtering. Tungsten oxide is selected as an electrode because it is a promising electrochromic material. The capacity of switching optical properties in response to applied voltage is a key property for electrochromic materials. The optical states switch when the voltage is applied to the WO_3 films. In other words, the transmittance is altered in a persistent and reversible way by intercalation and deintercalation of small cations such as H^+ and Li^+. Tungsten oxide film is colored and bleached by insertion and removal of the cations inside the WO_3 crystal structure. The reaction mechanism is explained as:

$$\underset{\text{(Bleached state)}}{WO_3} + xe^- + xM^+ \leftrightarrow \underset{\text{(Colored state)}}{M_xWO_3}\,(M=Li,H) \qquad (3.1)$$

Electrochromic behavior depends on the deposition technique which is magnetron sputtering and growth parameters. Here the deposition parameters are given in Table 3.7.

Table 3.7 Deposition parameters of WO_3 via magnetron sputtering.

I.D	Power (W)	Sputter Pressure (Pa)	Base Pressure (Pa)	Rate	Ar/O_2 Percentage (%)	Ar/O_2 (sccm)	Rotation (rpm)	Time (h)
W01	45	1.3	$7.9x10^{-8}$	0.3	50/50	2.6/2.6	5	2.0
W02	60	1.9	$9.8x10^{-8}$	0.5	50/50	2.8/2.8	5	3.0
W03	60	1.3	$1.1x10^{-7}$	0.6	50/50	3.1/3.1	10	2.5
W04	45	1.9	$1.1x10^{-7}$	0.4	50/50	2.6/2.6	10	2.0

WO_3 thin films are deposited at room temperature. In our case WO_3 electrodes are prepared via magnetron sputtering and according to the thickness monitor of the sputter the thickness for both of the metal oxides are approximately 150 nm.

3.7.3 NiO

Nickel oxide (NiO) films were deposited on top of ITO coated glasses by magnetron sputtering. . Magnetron sputtering is a well-established technique for electrochromic (EC) applications. NiO possesses anodic electrochromism. During the coloration mechanism the film switches between transparent and brown upon extraction and insertion of charge. By incorporating cathodically coloring WO_3 films and the ion conducting electrolyte part, the EC device structure becomes complete. The films were produced from metallic Ni target under Ar/O_2 environment. Electrochromism of NiO and electrochromic device performance containing tungsten oxide, nickel oxide and lithium conducting electrolytes are widely studied due to its promising nature and extensive use. NiO is an effective electrochromic material due to its good cyclic reversibility. The anodic electrochromism leading to coloration (proton insertion/extraction) proceeds via the following reaction: (Yang et al., 2016)

$$NiOOH + H^+ + e^- \leftrightarrow (NiOH)_2 \qquad (3.2)$$

(Colored state) (Bleached state)

Table 3.8 Deposition parameters of NiO via magnetron sputtering.

I.D	Power (W)	Sputter Pressure (Pa)	Base Pressure (Pa)	Rate	Ar/O_2 Percentage (%)	Ar/O_2 (sccm)	Rotation (rpm)	Time (h)
N01	90	2.0	$1.3x10^{-3}$	0.88	35/65	3.6/6.8	5	2.0
N02	100	1.6	$1.3x10^{-3}$	0.76	35/65	3.2/6.9	5	2.5
N03	120	2.0	$4.2x10^{-3}$	0.65	35/65	3.5/6.6	5	2.0
N04	90	1.6	$3.3x10^{-3}$	0.8	35/65	3.3/6.8	5	2.0

NiO thin films are deposited at room temperature. NiO thin films are both coated with magnetron sputtering and e-beam evaporation technique. With e-beam, a double layer structure is formed (YHO/NiO). With magnetron sputtering NiO is deposited on ITO. Eventhough NiO is coated for different purposes (photochromic/electrochromic) on different substrates, e-beam evaporation technique was much faster than magnetron sputtering. In both deposition conditions the coatings were uniform and homogenious.

4. ELECTROLYTE LAYER: LIPON

Energy storage is vital for current technologic devices. Li-ion batteries have many applications as a portable energy source so it is a very popular and important research topic. In order to improve the properties of the battery, the electrolyte layer plays a key role and it should be optimized. LiPON is a compound known as lithium phosphorusoxynitride which is used as a solid state electrolyte. LiPON, an amorphous solid state electrolyte for lithium ion batteries, has received attention since its discovery by Bates et al. in 1992 (Nowak et al., 2015). It is produced from Li_3PO_4 targets under N_2 atmosphere via RF (radio frequency) magnetron sputtering technique (*Microfilmed 2003*, 2003). Although there is progress in terms of enhancing the conductivity of solid electrolytes, liquid electrolytes are still widely used for electrochemical systems. Solid state batteries can overcome some of the some problems of liquid electrolyte batteries, being less hazardous and having a less flammable electrolyte-electrode system and better storage capacity (J. G. Kim et al., 2015). There are basic requirements for a suitable electrolytes for electrochemical devices are high ionic conductivity, low melting and high boiling points, chemical and electrochemical stability, and safety. The most important ones are electrolyte conductivity and electrochemical stability when it comes to selecting an electrolyte for modern electrochemical devices such as advanced batteries, fuel cells, super-capacitors, sensors, and electrochromic displays ("Electrolytes," 1953). Durability is a very important concept, for electrochromic applications. Lithium ion based all inorganic thin film structures may present advantages regarding physical and electrical durability. For Li^+ based devices, the ion conducting layer is a thin film material which allows rapid transfer of Li^+ between electrochromic layers without transporting electrons between them. In our case, this material is LiPON thin film. Ion conductivity determines the optical performance of the multilayer device structure. Therefore, the fabricated LiPON films are investigated in terms of their Li^+ conductivity and electronic conductivity. The ion conducting layer should have a high Li^+ conductivity

which is smaller than 10^{-7} Scm^{-1}. The ion conducting layer should have a high optical transmittance in the considered spectral range (Oukassi et al., 2016). LiPON films exhibit many advantages such as, good electrical and physical durability especially under a wide range of temperatures or ultraviolet radiation. Li based electrolytes have a similar working principle with lithium ion batteries, during charging/discharging processes they can change their optical properties. At some sources LiPON shows very good electrochemical stability with a good ionic conductivity up to 10^{-6} Scm^{-1} at room temperature (Xiao et al., 2018). The films which are produced by magnetron sputtering suffers from low deposition rate compared to other techniques because the deposition rate is~2 nm/min (Y. G. Kim, 2008). In this work, LiPON electrolytes are obtained via magnetron sputtering in various different deposition condition. These conditions and their outcomes will be mentioned in this chapter. During RF magnetron sputtering the selected target is cold-pressed and sintered Li_3PO_4 targets. Sputtering conditions have a huge influence on the conductivity and the physical and chemical properties of LiPON films. The most important parameters which are mentioned in the literature are pressure of N_2 (Fleutot et al., 2011), power density (RF)(Nimisha et al., 2011), deposition rate, composition of the target(West et al., 2016), target density(Hamon et al., 2006) and target to substrate distance (Su et al., 2015).At this thesis, LiPON is prepared under different N_2 and O_2 atmosphere and RF powers with magnetron sputtering. Li_3PO_4 ceramic target is used for the deposition and the substrate was Ag coated glass. The target to substrate diameter is kept 15 cm. Before the deposition the target was pre-sputtered under Ar atmosphere for 20 minutes to remove the possible surface contamination. The chamber was evacuated to 10^{-3} Pa. The sample holder rotated uniformly to obtain homogeneous thin films.

The ionic conductivity of LiPON is determined by AC impedance measurement. An AC voltage with the amplitude of 300 mV is applied to Ag/LiPON/Ag sandwich structure. The frequency ranged from 5000 Hz to 1MHz. The electrode area is 0.2 cm^2. The LiPON film thicknesses change and they will be mentioned further. The thicknesses are measured by a profilometer. The ionic conductivity, σ, was calculated from the following equation 4.1:

$$\sigma = (1/R)x(d/A) \qquad (4.1)$$

Where d is the solid electrolyte thin film thickness (cm), A the area of the electrode (cm^2) and R the solid electrolyte thin film resistance (Ω) deduced from the Nyquist diagram (Fleutot et al., 2011).

LiPON films are done with different RF power are investigated in terms of their ionic conductivity. The Ar, N_2, O_2 gas percentages are 38, 50, 12 respectively. The other parameters are given in the Table 4.1.

Table 4.1 LiPON magnetron sputtering parameters.

Sample I.D.	Power (W)	Thickness (nm)	Deposition time (h)
N477	60	584	8.5
N476	95	1140	7
N473	125	732	4.5
N472	160	920	4
N475	200	882	3

The parameters for calculating the ionic conductivity (σ) is given in the Table 4.2

Table 4.2 Parameters for calculating the ionic conductivity.

Sample I.D.	R (ohm)	Surface area (cm^2)	σ (Scm^{-1})
N477	18000	0.19	$1.6x10^{-8}$
N476	23630	0.19	$2.4x10^{-8}$
N473	10960	0.19	$3.4x10^{-8}$
N472	2800	0.19	$1.6x10^{-7}$
N475	6400	0.19	$7.0x10^{-8}$

R is the resistance determined from the impedance fitting. The Nyquist spectrum of the LiPON film between Ag electrodes have high and low frequency ranges. At high frequency range, which defined between 1 MHz^{-5} and 10^3 Hz, the semicircular relationship of impedance and frequency demonstrates electrolyte bulk effect (Xiao et

al., 2018). The diameter of the semi-circle correlates with the resistance of LiPON layer. The resistance (R) that is selected for the ionic conductivity formula is found by fitting the Nyquist spectrum with an equivalent circuit model. At low frequencies, the linear segment with a constant phase angle attributes to the polarization impedance at LiPON/Ag interfaces.

4.1 Characterization of LiPON

For LiPON electrolyte coating there are 3 different characterization techniques which is used at this thesis. XRD, SEM and FTIR is used to understand the crystal structure, chemical structure and morphology of LiPON. The analysis from these characterization techniques will be mentioned at this section.

XRD technique investigates the cystalline structure of the material by using x-rays to measure the diffractions from the planes of the crystal structure. XRD is also used to measure the crystalline content of coated materials. The crystalline phases and their quantities of mixtures in favorable cases are identified to determine the spacing between lattice planes. XRD analysis of LiPON films are shown in Figure 4.1.

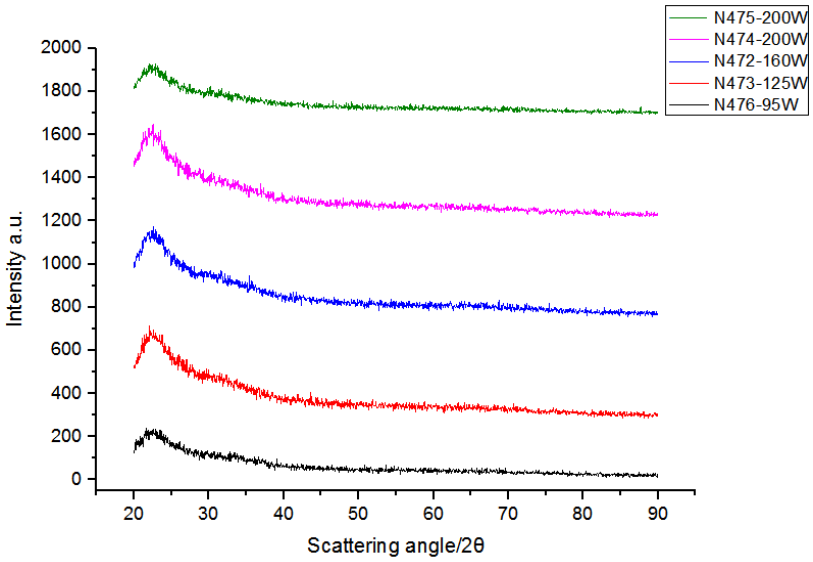


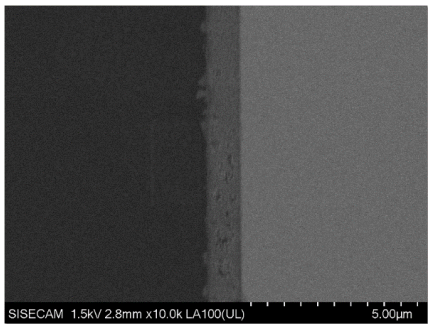
Figure 4.1 XRD analysis of LiPON thin films.

From XRD, It can be observed that there is no definable peak. The reason behind this could be that the thickness of LiPON coating was not enough to get any peaks because glass is amorphous. There is a hump at 2θ = 18-35 (for all of the samples) which

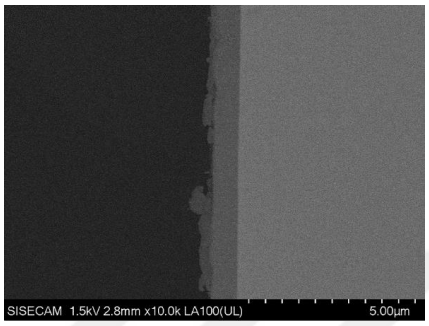
corresponds to silica. Our samples have very low thickness and the X-ray will easily penetrate the film and up to the glass slide.

SEM is a materials characterization tool used for basic materials research, quality control and mechanical failure analysis. It has a key role for examining metals, alloys, ceramics and polymers. SEM images of the samples is used for imaging the morphology of the LiPON coating to Ag. Ag is coated to glass as an electrode contact and to see the cross section behavior of LiPON on a conductive layer. The SEM images are given in Figure 4.2 down below:

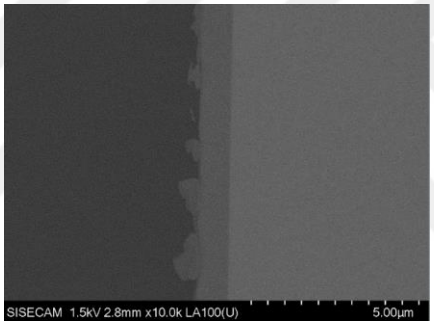
a)



b)



c)



d)

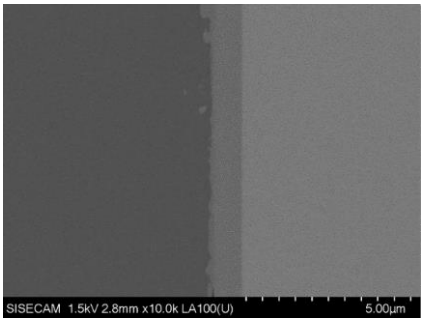


Figure 4.2 Cross section SEM analysis of a) N472, b) N474, c) N473, d) N475.

The darker part (on the left) represents Ag and the mid section which is lighter is LiPON. As it can be seen in all cases, at the Ag LiPON interphase the surface is not homogeneous. If the temperature was high, it could be said that there was an interface

diffusion between the electrode and electrolyte layer. Interface diffusion along a metal/ceramic interface is seen in many electronic devices and it has an effect on stability of the device. There is an extensive literature exists on the, atomic structure, and chemical composition of metal/ceramic interfaces. On the other hand, there is very little information about atomic diffusion along this channel. Diffusion of crystal defects (dislocations, and grain boundaries) is generally faster than bulk diffusion (Kumar et al., 2018).

Figure 4.3 presents the FTIR patterns of LiPON. Even if the samples are coated with different powers. There isn't any significant signals.

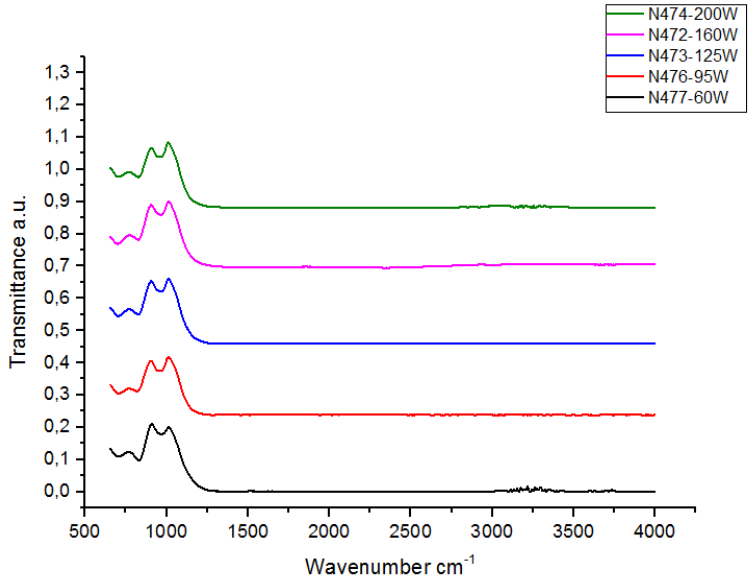


Figure 4.3 FTIR analysis of LiPON films.

FTIR analysis monitors chemical compounds and identifies chemical bonds by detecting the functional groups present at distinct bands. FTIR is an effective analytical instrument for covalent bonding information. In our case, as it can be seen at the graph, there is no definable peak after 1000 cm^{-1}. This peak corresponds to the silicate ion which comes from the glass substrate.

5. CONCLUSION

- NiO, SiO_2, TiO_2 and Al_2O_3 are coated with e- beam deposition on top of YHO coated glass. In order to have a control group the coatings are also made on top of glass. Each deposition is optimized as a transparent and homogeneous layer so that we can observe the photochromic property of MO_x encapsulated YHO.
- In each trial the parameters which made the most difference were deposition rate, oxygen flow and thickness. A total of 4 sets of experiments were carried out for each metal oxide. The samples that are most successful in observing the optical properties were found. For the MO_x coated YHO the optimized parameters are given down below:
- For NiO, deposition rate is 0.5A/s, O_2 flow is 10 sccm and the film thickness is 150nm. For SiO_2, deposition rate is 0.5A/s, O_2 flow is 12 sccm and the film thickness is 100nm. For TiO_2, deposition rate is 0.5A/s, O_2 flow is 10 sccm and the film thickness is 100nm. For Al_2O_3, deposition rate is 0.5A/s, O_2 flow is 10 sccm and the film thickness is 100nm.
- Al_2O_3 and SiO_2 encapsulated YHO's long cycle optical transmission performed better than only YHO coated glass. This shows that the PC property of YHO is open to development.
- For coating PVB and PVP, the polymer solutions are prepared as 1, 5 and 10 weight percent. The optimum solution is 10 weight percent. Each solution is solved in 1 ml of ethanol and for PVB 126.99 mg and for PVB 133.685 mg of polymer powder is used. The spin coating rotational speed is changed between 500 rpm to 3000 rpm. For maximum coverage of the surface 2000 rpm is selected.
- When we look at the long-term transmittance performance of PVP and PVB coated YHO films, PVB coated YHO preserves its transmission for a longer period of time.

- Overall by looking at these results it is found that by encapsulating with metal oxides and polymeric thin films the long-life performance can be even more improved than only YHO coating. In the future, other types of metal oxides and polymers may be tried to see if the performance could be even better.
- WO_3 and NiO are also deposited by magnetron sputtering technique on top of ITO coated glass.
- A solid LiPON electrolyte has been developed by magnetron sputtering technique.
- As a solid electrolyte layer, LiPON can be a preferred material for the forthcoming applications. It can be reported that when the properties are tuned accordingly LiPON will be useful in future advances in solid-state battery system.

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