FABRICATION OF SMART GLASS ELECTROCHROMIC DEVICE
USING RF MAGNETRON SPUTTERING

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ABSTRACT

Electrochromic device is an important functional device to control the amount of light through a glass. It usually used in sunlight control window glazing for buildings and automobile. The important feature of electrochromic glass is the ability to response toward the apply voltage in shortest time, and endurance to maintain in color shape after apply voltage. In this thesis, the oxygen gas percentage is optimized during the fabrication of tungsten trioxide (WO$_3$) as an electrochromic glass for window glazing application by using RF magnetron sputtering. The oxygen flow rate for the deposition is varied from 10sccm -22sccm which is 25%, 27%, 30%, and 35% of oxygen flow. The structures of WO$_3$ were investigated using X-Ray diffraction, Field effect scanning electron microscopy (Fe-Sem) and Atomic force microscopy (AFM). The electrochromic properties were characterized by a cyclic voltammogram and UV-Vis absorption spectra. The results show that nanocrystalline film with particle size of 51.54nm was deposited at 27% oxygen flow rate has the largest charge capacity and coloration efficiency among the others. The time respond taken for complete coloration at 4V is 2second. This result is a starting point for future work such as optimizing the film thickness or doping by other metals.
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<td>Rh</td>
<td>Rhodium</td>
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<td>Ir</td>
<td>Iridium</td>
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<td>CVD</td>
<td>chemical vapor deposition</td>
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<tr>
<td>LiClO₄</td>
<td>Lithium perchlorate</td>
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<td>PC</td>
<td>Propylene carbonate</td>
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<td>NiOOH</td>
<td>Nickel oxyhydroxide</td>
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<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
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<td>NaOH</td>
<td>Sodium hydroxide</td>
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<td>IZO</td>
<td>Aluminum doped zinc oxide</td>
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<td>FTO</td>
<td>Fluorine-doped tin oxide</td>
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<td>FE-SEM</td>
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CHAPTER 1

INTRODUCTION

1.1 Introduction to electrochromic material

Electrochromic (EC) glass is a device that can change color when apply some voltage to the film. EC device consist of two EC layers separated by an electrolytic layer, conducting electrodes are used on both EC layers. Figure 1.1 show the basic structure of EC device embodies six superimposed layers on two substrates. First substrate consists of four layers as working electrode and the other substrate consist of two layers acting as counter electrode. Both substrates are then separated by electrolyte in a laminated configuration.

Working electrode usually made from mixed conductor, it acting as ion-storage layer and conduct ions and electrons. Optical absorption occurs when electrons move into the EC layers from the transparent conductors along with charge balancing ions entering from the electrolyte.

Figure 1.1: Electrochromic device configuration consist of two substrates divided by electrolyte.
Electrochromic (EC) becomes a whole wide attention among scientists since 40 years ago. However, electrochromism has remained an active area for basic and applied research, with large possibilities for applications in emerging technologies. The interest was boosted in the mid-1970s with the realization that electrochromisms was of much interest in fenestration technology as a means to achieve energy efficiency in buildings [1]. The application of electrochromic smart glass include transmittance modulation of sunlight control window glazing for buildings, optical display, and reflectance modulating automobile rear view mirrors [2].

Figure 1.2: Electrochromic Smart window used in a bulding [3]

Electrochromic (EC) materials are able to change their optical properties by changing the electrical voltage supply. Transition metal such as tungsten trioxide (WO$_3$), nickel oxide (NiO), molybdenum trioxide (MoO$_3$), and iridium trioxide (IrO$_3$) have been widely studied for used in electrochromic materials [4]. The electrochromic (EC) material will change their optical properties when charge insertion and this may cause the material change color or its opacity. Materials that change color upon insertion are called cathodic while a material that change color upon extraction called anodic. Metal oxide of W, Ti, V, Nb, Ta and Mo exhibit cathodic electrochromism and oxides of V,
Cr, Mn, Fe, Co, Ni, Rh and Ir are anodic electrochromism [5]. An amount of voltage needed to change its opacity, however once the glass change color, no electricity is needed for maintaining the particular shade which has been reach.

Method for preparing this electrochromic films include sputtering, spray pyrolysis, chemical vapor deposition (CVD), electrodeposition and sol-gel deposition. Figure 1.3 show the general schematic for spray pyrolysis, spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated surface, where the constituent react to form a chemical compound. The chemical compound is volatile at the temperature of deposition. The process is a particularly useful for the deposition of oxides and has long been a production method for applying a transparent electrical conductor [6].

![General schematic of a spray pyrolysis deposition process](image)

Figure 1.3: General schematic of a spray pyrolysis deposition process [7]
Chemical vapor deposition (CVD) is a chemical process used to produce high quality, high-performance, solid materials. The majority of its applications involve applying solid thin-film coatings to surfaces, it has been used to deposit a very wide range of materials. CVD also has a number of disadvantages. One of the primary disadvantages lies in the properties of the precursors. Ideally, the precursors need to be volatile at near-room temperatures [8]. Figure 1.4 illustrated the general process of CVD.

![Figure 1.4: General schematic of chemical vapor deposition process [9].](image)

Among those methods, reactive magnetron sputtering widely used to obtain WO$_3$ with good electric flow and optical properties. Sputtering is the process when an atom with enough energy bombarded into particles and produces an ion. The momentum transfer from the particles to the surface atoms can impart enough energy to allow the outer electron to escape from its orbit. Once ejected, these ion can travel to a substrate and deposit as a film. So in sputtering, the target material and the substrate is placed in a vacuum chamber. A voltage is applied between them so that the target is the cathode and the substrate is attached to the anode.
Plasma is created by ionizing a sputtering gas, generally a chemically inert, heavy gas like Argon. Figure 1.2 illustrate ionization process that creates plasma, the sputtering gas which is Argon ion will bombards the target and the target ion will deposit into substrate. Ions can be generated by the collision of neutral atoms with high energy electrons. The interaction of the ions and the target are determined by the velocity and energy of the ions, since ions are charged particles, electric and magnetic fields can control these parameters. The process begins with a stray electron near the cathode is accelerated towards the anode and collides with a neutral gas atom converting it to a positively charged ion. The process results in two electrons which can then collide with other gas atoms and ionize them creating a cascading process until the gas breaks down.

Figure 1.5: plasma ionization created during fabrication of Magnetron sputtering process [10].
The breakdown voltage depends on the pressure in the chamber and the distance between the anode and the cathode. At too low pressures, there aren’t enough collisions between atoms and electrons to sustain plasma. At too high pressures, there so many collisions that electrons do not have enough time to gather energy between collisions to be able to ionize the atoms.

1.2 Problem statement

An attempt to fabricate a high efficiency electrochromic glass using tungsten oxide WO$_3$ is increasing extensively due to high color efficiency study by researchers. However, the electrochromic films cannot change color simultaneously in time even though the film is supposed to change, most of the electrochromic devices are completely change color after 15 minutes [24]

1.3 Motivation

By changing the oxygen percentage would create defect in the WO$_3$ structure, and changing the performance of electrochromic device.

1.4 Objectives

Objective for this research is to fabricate electrochromic thin film using tungsten target using RF magnetron sputtering method and LiClO$_4$+PC as electrolyte. Oxygen flow of RF magnetron sputtering chamber was change to improve the performance of the device.

This research embarks on the following objectives:

a) To fabricate a fast color response of electrochromic WO$_3$ thin films

b) To get a low transmittance for blench state and color state of films after test voltage.
1.5 Scope of project

The main scope of this project is to investigate characterization of tungsten trioxide as electrochromic material. The scopes include:
1. To fabricate WO₃ film using pure 99.99% tungsten target using RF magnetron sputtering
2. To change parameter of oxygen flow to get high efficiency based on time respond of electrochromic WO₃ thin film.
3. To investigate the properties of WO₃ thin film deposited at various oxygen flow by using FE-SEM, AFM, XRD and two point probe.

1.6 Thesis Organization

This thesis consist of five chapter, the first chapter of this thesis consist of introduction to electrochromic material, this part explained about general overview of electrochromic smart glass based on first discovery, application and suitable material to produce this smart glass. Next section is about background study, problem statement, objectives, motivation, and scope of project and thesis organization. Second chapter is literature review consist of History, principle operation of electrochromic trioxide (WO₃) development, WO₃ thin films properties, and RF magnetron sputtering system. For third chapter, it consist of methodology on fabricating the WO₃ thin film using RF magnetron sputtering and introduce to the apparatus used to measure the characteristic of WO₃ materials. Chapter four consist of discussed about result and discussion of experiment and the last chapter is about conclusion to this research and future recommendation for future good. This thesis ended by references used during this research and Appendix for this thesis.
CHAPTER 2

LITERATURE REVIEW

This chapter consists of historical method and technology development for preparing electrochromic thin films, fabrication method, tools, and characterization equipment. This chapter may help to understand this project through basic theory.

2.1 History

Smart glass or switchable glass also called smart windows or switchable windows, it is refer to glass that changes light transmission properties under the application of voltage, heat or light. The glass blocking certain or all wavelength of light to pass through and it change into two conditions which are colored or blenched. Smart glass technologies include electrochromic, photochromic, thermochromic, suspended particle, micro-blind and liquid crystal devices [11] become interested among researcher.

The basic concept behind all smart windows is the same, they can be made in several different ways, each with a different method and properties for blocking light. Critical aspects of smart glass include material costs, installation costs, electricity costs and durability, as well as functional features such as the speed of control, fastest response, possibilities for dimming, and the degree of transparency.

An electrochromic window has a double-sandwich of thin layers, a separator in the middle, two electrodes act as electrical contacts on either side of the separator, and then two transparent electrical contact layers on either side of the electrodes. The basic working principle involves lithium ions acting as positively charged lithium atoms with
missing electrons that migrate back and forth between the two electrodes through the separator.

Normally, when the glass is clear, the lithium ions reside in the innermost electrode. When a small voltage is applied to the electrodes, the ions migrate through the separator to the outermost electrode where they scatter away most of the incoming light and turn the glass opaque. They remain there by themselves until the voltage is reversed, causing them to move back so the glass turns transparent once again. This process can be illustrated by figure 2.1 below. The power only needed to change them from one state to the other and no power is needed to maintain the windows in color or opaque state. The general EC phenomena of WO₃ due to the formation of tungsten bronze (MₓWO₃) according to the equation below where M⁺ is H⁺, K⁺, Li⁺, or Na⁺.

\[
WO₃ + xM^+ + xe^- \rightarrow M_xWO₃
\]

(Transparent) \quad (blue)

Figure 2.1: How electrochromic glass work
When installed in the envelope of buildings, smart glass creates climate adaptive building shells, with the ability to save costs for heating, air-conditioning and lighting and avoid the cost of installing and maintaining motorized light screens or blinds or curtains. Most smart glass blocks ultraviolet light, reducing fabric fading.

2.2 Background study

EC material was found since early 1970 by researcher, researcher early found that evaporated tungsten trioxide amorphous layers commonly used in EC displays actually have the composition WO2.7Hy (0.2<y<0.5). Then researcher emphasize that coloration of virgin transparent films can be obtained without injection of any external ion into the layer [12]. Tungsten trioxide WO₃ widely treated as electrochromic (EC) material because of it has rich special physics and chemical properties [13], photochromic [14,15], gasochromic [16], catalyzed [17], and hide material [18], and it even has potential as a superconducting material [19]. Researchers nowadays are focused on WO₃ (coloring under charge insertion) this is due to the advantage among the others in terms of reversibility, stability and color efficiency.

Tien-syh Yang in his paper said some crystallization dispersed in the WO₃ thin film possesses the better coloration efficiency. Larger internal volume with optimal nanocrystal-size is essential to conduct ions and electrons for electrochromic intercalation [20]. On the other hand, Hiroharu Kawasaki in his paper said, in general, the amorphous WO₃ thin film has a good performance as an electrochromic display. Some sample deposited at different parameter using same magnetron sputtering method. Figure 2.2 explained at total gas pressure 3 Pa, a crystalline WO₃ (022) peak can be observed. With increasing total gas pressure, the crystalline peaks disappear that means the films are amorphous. [21].

Apart from that, C. Chananonawathorn believe that amorphous WO₃ films are more suitable than crystalline WO₃ films for electrochromic applications. A crystalline structure is less favorable for ions to diffuse through because of the densely packed atomic structure, because the lithium ion movement through the film is obstructed by the
dense structure leading to a lower response time. Figure 2.3 shown WO$_3$ films were poor crystallinity or amorphous structure shown at different deposition oxygen flow rate for 5sccm, 10sccm, 15sccm and 20sccm. However, these amorphous or nanocrystalline structure of WO$_3$ films resulted in better electrochromic property than crystal structure [22].

Figure 2.2: XRD patterns of the WO$_3$ films deposited using the W target on the glass substrate. RF power: 50W, O$_2$: Ar =5:5 [15].
The transmittances at 550nm usually observed due to visible spectrum (400nm-700nm) where for Violet, Indigo, Blue, Green, Yellow, Orange and Red for 400nm, 445nm, 475nm, 510nm, 570nm, 590nm, 650nm respectively. The best transmittance should be higher than 80% and below 80% after gives some voltage.

Furthermore, electrolyte effect was study by researchers, different type of electrolyte will give different color to the film. Usually researchers used NiOOH [23], HCl, NaOH, and LiClO₄. Among this electrolyte LiClO₄ become concentration among researcher, this is due to the fast chemical reaction. The color of the films changes to dark blue when positive Lithium ions and electron are electrochemically injected into these films [24-26]. The films reported show a good coloration behavior in the visible and NIR region when it was deposited at 60% oxygen content, it show a good electrochromic stability as Li⁺ ion can be almost inserted and extracted reversibly and good reverse phenomena between the coloration and blenchd state [27].

Other than that, in theory band gap energy for bulk WO₃ is about 2.62eV. The maximum optical band gap of 3.14eV was reported for the film deposited at 3.1 x 10⁻²
mbar, and it decreased by decreasing oxygen sputter pressure. The lowest band gap was reported is 2.97 at bleached state at 1.5 x 10^{-2} mbar [28]. The best EC film is having a short response times below 1 minute and it can be achieved by obtained optimum band gap energy. The crystalline reported to be increase by increasing temperature, however the response for electrochromic at room temperature is faster than at temperature 500°C.

2.3 Principle operation of electrochromic thin films

Electrochromic is materials which are changing color reversibly when they kept in a different electronic state through either by reduction (absorbing electrons) or oxidation (loosing electrons). The phenomenon of color change is called electrochromism. Electrochromic materials are divided into different groups by their physical state at room temperature. In this way electrochromic materials are divided into 3 broad categories. The first category has electrochromic materials that are soluble in neutral states even after electron transfer. Examples of such a compound are Molecular dyes (ethyl viologen). Second category has electrochromic materials that are soluble in neutral state and forms solid on electrode surface (which is insoluble) after the electron transfer, for example heptyl viologen.

Third category has electrochromic materials that are solids in neutral state and remain in solid state after the electron transfer. Examples are metal oxide films and conducting polymers. This system can be viewed as rechargeable electrochemical cell in which electrochromic electrode(where oxidation reduction takes place) and charge balancing counter electrode are separated by solid electrolyte (generally polymeric) or liquid electrolyte. Color changes in these devices occur by charging and discharging of the cell on application of electricity [29].

When a voltage is applied on EC thin films, ions are inserted into WO_3 film in the device, thereby the optical properties are changed. It switches reversibly from transparent to dark blue upon electrochemical redox reactions. The insertion/extraction process can be represented by:

\[ \text{WO}_3 \text{ (transparent)} + x\text{Li}^+ \text{(or H, Na, K)} + xe^- \Leftrightarrow \text{Li}_x\text{WO}_3 \text{ (blue)} \]
This reaction goes to the left or right depending on the sign of the applied voltage. When ions are inserted, both XPS and electron spin resonance (ESR) show that W5+ as well as W6+ is present, and that the W5+ density scales with the intensity of the EC absorption peak [30].

![Diagram of electrochromic process](image)

Figure 2.4: Schematic structure of the electrochromic process in electrochromic (EC) and ion movement during coloration process.

2.4 WO₃ thin films properties

WO₃ shows different crystal structures at different temperatures. The most common monoclinic crystal structure of WO₃ is represented in Figure 2.5. There is another stable tungsten oxide compound, also existing in the tungsten-oxygen shape.
Electrochromic device employ both amorphous as well as crystalline WO$_3$ film owing to their highly catalytic behavior both in oxidation and reduction processes. The amorphous films have their applications in transmittance modulation devices in the visible region, whereas the crystalline WO$_3$ film, due to its better reflection modulation in near-infrared region of the spectrum, is used for thermal modulation. The coloration in WO$_3$ thin film occurs due to ionic insertion but the coloration mechanism in crystalline WO$_3$ films is different from amorphous thin films.

Figure 2.6 shows XPS spectra of evaporated W oxide films intercalated to different values of x from work by Hashimoto and Matsuoka [32, 33]. The intensity goes towards zero at higher energy, but then a narrow peak appears just below the Fermi level. This peak increases with the amount of ion intercalation. The reason for this feature is probably that the electrons that are inserted together with the ions occupy the lower part of the conduction band. The minimum between the two peaks corresponds to the band gap.
The optical properties of the various electrochromic materials differ substantially. Since tungsten oxide is the most common material that deal with it in more detail than the other materials. Upon the insertion of small positive ions for example protons, Li+, K+ or Ag+ , tungsten oxide absorbs light with a maximum around 950 nm. This gives rise to a deep blue color of the material. The disorder in the material is large enough to cause localization of the injected electrons. The optical properties can be understood using small polaron theory crystalline tungsten oxide has a higher lattice order which give rise to a more free-electron like behavior [34]

In contrast the tungsten oxide film absorbs most in the visible part of the spectrum. This results in a greyish to bronze color. Prussian blue has optical properties that are close to amorphous tungsten oxide, with the big difference that it colors when the ions are removed from the film. It can be combined with tungsten oxide in devices where both layers color or bleach at the same time [35]
2.5 RF Magnetron Sputtering method

Recent years, variety method and techniques were used to fabricate electrochromic thin film as a smart glass or smart window using different material such as V$_2$O$_5$-z [36], IZO [37], Nb$_2$O$_5$ [38], fluorine-doped tin oxide (FTO) [39], NiOx [40,41], Nb$_2$O$_5$:MoO$_3$ [42], and tantalum oxide [43]. Some method to fabricate electrochromic thin films include sol gel chemistry [44], solid-state metal-oxide-metal capacitor development [45], poly(3,4-ethylenedioxy-thiophene)(PEDOT) [46], magnetron sputtering [47,48], layer by layer assembly (lbl) [49], and chemical vapor deposition [50].

W. R. Grove was the first person to study about sputtering process on 1852 whereas others had observed the effect while studying glow discharges. Since that most of the physical vapour deposition is closely associated with the development of vacuum technology, the first piston type vacuum pump was invented by Otto van Guericke at 1640 in order to pump water out of mines. However, the first person to apply the vacuum pump in order to form a glow discharge in a vacuum tube was M. Faraday in 1838. Since then, magnetron sputtering was studied by several researcher and the first uses of radio frequency (RF) to sputter material was investigated in the 1960s [51].

In 1966, Davidse and Maiseel used RF sputtering to produce dielectric films from dielectric materials. However, RF sputter deposition is not used widely due to their high cost and the introduction of high temperatures, due to the high self-bias voltage associated with RF power. RF sputtering was then developed to sputter de-posited hard coatings on tools at mid-1970s and became commercially available at early 1980s [52]. Magnetron sputtering is a technique that requires a high energy of ions for bombardment, amounting to a few hundred of electron volts around the cathode. Due to the bombardment of the ions towards the cathode, fast metal atoms are formed along with secondary electrons. Basically, during the sputtering process, gas ions at the plasma were accelerated towards the target material that to be deposited. The material will then detached from the target and deposited on the substrate.

Basically, the advantages of reactive sputtering compared to chemical vapor deposition, reactive DC sputtering and sol-gel chemistry techniques is due to reactive sputtering deposit thin film at low deposition rates and the oxygen content can be
controlled to produce specifically. Other than that, the sputter deposited films have a composition close to that of the source material. The difference is due to different elements spreading differently because of their different mass (light elements are deflected more easily by the gas) but this difference is constant.

Figure 2.5: Ionization process in Magnetron sputtering chamber during fabrication.

Sputtering is the process ion or atoms from inert gas bombarded into metal surface and produce a metal ion. The movement of an ion illustrated in figure 2.4. The ejecting material from a target will be depositing on a substrate such as a silicon wafer, glass, Indium Tin Oxide (ITO) and Fluorine doped Tin Oxide (FTO) Substrates are placed in a vacuum chamber and are pumped down to a prescribed process pressure. Sputtering starts when a negative charge is applied to the target material causing a plasma or glow discharge. Positive charged gas ions generated in the plasma region are
attracted to the negatively biased target plate at a very high speed. This collision creates a momentum transfer and ejects atomic size particles from the target. These particles are deposited as a thin film into the substrates surface [53].

Sputtering is extensively used in the semiconductor industry to deposit thin films of various materials in integrated circuits processing. Thin anti reflection coatings on glass, which are useful for optical applications are also deposited by sputtering. Because of the low substrate temperatures used, sputtering is an ideal method to deposit contact metals for thin film transistors. This technique is also used to fabricate thin film sensors, photovoltaic thin films (solar cells), electrochromic thin films, metal cantilevers and interconnects.
CHAPTER 3

METHODOLOGY

This chapter describes the method used to fabricate thin films, it emphasize on procedure and process carried out during preparation and fabrication of electrochromic thin film.

3.1 Introduction

In this research, RF magnetron sputtering technique was used to fabricate WO₃ thin film. During the process, a 99.99% tungsten metal was used as a sputtering target and ITO glass with sheet resistance 180Ω/cm² as a substrate. Several parameters were fixed while oxygen parameter changed during fabrication process. The WO₃ thin film will be analyzed using surface analysis equipment such as field emission scanning electron microscope (FE-SEM), atomic force microscope (AFM), X-Ray diffraction (XRD), UV-Visible Spectroscopy (UV-Vis), Alpha-Step IQ Surface Profiler, and two point probe(IV characteristic). The standardized process to analyzed and fabricate the WO₃ as electrochromic glass was according to the flow chart in figure 3.1.
Figure 3.1: Flow chart of the process for fabricating tungsten trioxide (WO$_3$) as electrochromic films.
3.2 Fabrication process

Tungsten trioxide (WO\textsubscript{3}) was constructed using RF magnetron sputtering to perform as electrochromic glass. Normally electrochromic films have two pieces of glass, overall it consist of 5 layers as shown in figure 3.2. The first piece of electrochromic thin film has 3 layers consist of glass and Indium Tin Oxide (ITO) as substrate to the film, followed by WO\textsubscript{3}. Second piece consist of Indium Tin Oxide (ITO) only. LiClO\textsubscript{4}+PC act as electrolyte and Au electrode was fabricated at both films using DC sputtering. First film act as working electrode and second film act as counter electrode.

Figure 3.2: Basic design of electrochromic device including LiClO\textsubscript{4}+PC electrolyte to transport ions.
3.2.1 Substrate cleaning process.

A 2×6cm Indium Tin Oxide (ITO) glass was cut using diamond cutter into 3 parts. Acetone and ethanol was used to clean the contamination on the ITO surface using ultrasonic bath in 10 minutes. The sample then dried in nitrogen gas flow. (see figure 3.3)

Figure 3.3: Equipment used to cleaning substrate process
3.2.2 Deposition

Step 1: Conductivity of ITO sample was checked using multimeter then ITO substrate plastered using heat resistant tape onto substrate holder on Magnetron sputtering

Step 2: Fabrication of WO$_3$ was started using Magnetron Sputtering machine (See figure 3.4) followed manual attached at APPENDIX.

![Magnetron sputtering](image1.jpg)  ![Sputtering chamber](image2.jpg)

Figure 3.4: Magnetron sputtering machine

To perform a better electrochromic material, several parameter needed was optimized. Oxygen flow rate was change from 25%, 27%, 30% and 35%. The parameter used to fabricate WO$_3$ thin films shown in table 1.
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