

**LUMINANCE AND COLOR OF GRATING SMART WINDOW
FOR PEDOT-Al₂O₃ BY ALGEBRAIC EIGENVALUE**

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Thesis
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LUMINANCE AND COLOR OF GRATING SMART WINDOW FOR PEDOT-
Al₂O₃ BY ALGEBRAIC EIGENVALUE

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ABSTRACT

A smart window is a window that can change its optical properties by the application of an electric field. We propose a new type of smart window, a grating smart window, by exploiting the periodic structure of Al₂O₃ and PEDOT, Poly(3,4-ethylenedioxythiophene) in an electrochromic layer. This thesis is a technical feasibility study of the grating smart window. We concentrate on the luminance and color indexes from the grating smart window. Those can be evaluated by converting from the light spectrum data. The commercial software GSolver is used to compute the transmitted spectrum (in the range of 380-750 nm) from the grating smart window. The spectra are converted through CIE XYZ colorimetry in order to find the color indexes which hold luminance information. Three grating types are investigated, one is single layer grating (A structure) and the others are double layer grating (B and C structure). The observed results are compared to that from a normal smart window. We found that when the PEDOT in the grating is in the transparent state (doped), the colors in the field of view from the gratings are rather homogeneous, like the normal one. In contrast, the dim state (neutral) shows various colors unlike the normal.

KEY WORDS: SMART WINDOW/ GRATING STRUCTURE/
THIN-FILM OPTICS/ COLORIMETRY

70 pages

ความสว่างและสีส้มของกระจกอัจฉริยะแบบมีเกรตติงที่สร้างจากพีคอตและอลูมิเนียมออกไซด์โดยใช้อัลจีบราอิกไอเกนแวลู

LUMINANCE AND COLOR OF GRATING SMART WINDOW FOR PEDOT- Al_2O_3 BY ALGEBRAIC EIGENVALUE

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บทคัดย่อ

กระจกอัจฉริยะคือกระจกที่สามารถเปลี่ยนสมบัติเชิงแสงของตัวมันเองได้โดยใช้สนามไฟฟ้า เราขอเสนอกระจกอัจฉริยะแบบใหม่คือกระจกอัจฉริยะแบบมีเกรตติงโดยใช้ประโยชน์จากโครงสร้างแบบเป็นคาบของอลูมิเนียมออกไซด์และพีคอตในชั้นของอิเล็กโตรโครมิกงานวิจัยชิ้นนี้ศึกษาความเป็นไปได้เชิงเทคนิคจากกระจกอัจฉริยะแบบมีเกรตติง โดยเน้นทางด้านความสว่างและสีส้มของมัน ค่าเหล่านั้นสามารถหาได้จากสเปกตรัมของแสง โปรแกรมคำนวณGSolver ถูกใช้เพื่อหาสเปกตรัมของแสง(380-850นาโนเมตร)ที่ผ่านกระจกอัจฉริยะแบบมีเกรตติง สเปกตรัมเหล่านั้นจะถูกเปลี่ยนเป็นดัชนีสีโดยผ่านกระบวนการ CIE XYZ ซึ่งรวมถึงค่าความสว่างด้วย ค่าเหล่านี้ต้องถูกเปลี่ยนเป็น sRGB อีกทีเพื่อที่จะให้มันแสดงผลบนหน้าจอคอมพิวเตอร์หรือจากเครื่องพิมพ์ได้ สีเหล่านั้นจะถูกนำไปวาดสนามแห่งการมองเห็นซึ่งมันจะบอกถึงภาพเมื่อผู้สังเกตมองไปยังกระจกอัจฉริยะแบบมีเกรตติง มีโครงสร้างเกรตติงสามแบบที่เราทำการศึกษาและนำมาเปรียบเทียบกับกระจกอัจฉริยะแบบธรรมดาด้วย เราพบว่าเมื่อพีคอตอยู่ในสถานะใส(ถูกโด้ป)สีของกระจกแบบใหม่ ค่อนข้างที่จะเป็นเนื้อเดียวกันคล้ายกับแบบธรรมดา มันเหมือนกับว่าแสงไม่ค่อยเลี้ยวเบนมากนัก ในทางตรงกันข้ามสถานะมืด(ธรรมชาติ)ปรากฏสีที่หลากหลายไม่เหมือนกับแบบธรรมดา

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LIST OF ABBREVIATIONS

n	Refractive index
k	Extinction coefficient
α	Absorption coefficient
σ	Optical conductivity
θ	An angle between z axis and ray
\emptyset	An angle between y axis and plane of incident
δ	Phase different
Y	Luminance

CHAPTER I

INTRODUCTION

A smart window is one type of windows that can switch its transparency from transparent state to darker or even opaque state upon the change of incident light intensity. Normally, the smart window is installed on houses, offices, vehicles or airplanes to reduce the glare of the sunlight to the personnel inside. Its application to a motorcycle helmet is also being investigated. It seems to be a future window.

Now a day, the smart window that changing between transparent-to-dim and transparent-to-diffuse are two main groups of smart window technology. For the transparent-to-dim one, the window absorbs much of the incident light and makes it appear dim. There are numerous ways to achieve such properties, e.g., by mean of electrochromic [1]–[3], micro blind [4], suspended particle display [1]–[3]. The transparent-to-diffuse one causes the light to scatter without absorbing, which cause the window to appear translucent. Liquid crystal window is one example to achieve this property [5]. There may be a new smart window type such as transparent-to-color. It may be constructed by exploiting the diffraction from a grating structure. Among of all current smart windows, the electrochromic type shows the most feasibility. It is because it can fabricate the periodic structure and that grating period is low in range of nanometer or micrometer [6]. It is enough to make the diffraction from the sunlight. A material will can be called electrochromic if it can change the color by the application of an electric field. However, some of them lack the transparent property which may not good for smart window application. We need to select the electrochromic with high transparent in one state and large absorbance in the other state. Additional functions are also of interest.

The electrochromic smart window was realized since 1930 [7]. It took a few decades before the first electrochromic window was made available commercially, i.e., by Satyen Deb in 1969, by using tungsten trioxide (WO_3) [8]. Some companies have their scientists and inventors follow this line of materials to produce the

switchable smart window since 1980. Other companies may have adopted the conductive polymer in place of tungsten oxide. The first conductive polymer in this line of smart window is poly(3, 4-ethylene- dioxythiophene) or PEDOT, which has first been synthesized in Germany [9]. Nowadays, this conductive polymer has some major advantages, i.e., (i) low power consumption (1-5 V) (ii) fast switching time, (iii) low require power on switching, and (iv) much lower cost on organic materials synthesis, but the disadvantage is short life time. The PEDOT and WO_3 are quite similar in their optical properties. The backbone of PEDOT is high brightness different between the transparent state (doped) and the dim state (neutral), and has faster switching time compare to WO_3 . PEDOT has its switching time in millisecond [10], and is rather easier to fabricate. Thus, these make the PEDOT very attractive choice.

However, PEDOT has only one color: blue. It lacks the variety in colors. PEDOT coating on the pre-designed grating structure is one way to overcome this shortage. A grating allows different colors (or wavelengths) from diffraction of different angle and allow rainbow tab on the grating. It makes the smart window more interesting. To make that, the material that used together with PEDOT should be the material that has optical properties different to dyed state of PEDOT; neutral PEDOT. However, if those properties are also different to bleach state of PEDOT; doped PEDOT, the rainbow tab also appears. It make the grating smart window less interest as transparent window, but it can avoid by find those properties similar to doped PEDOT. In such the way, the light will not be diffracted much, and the color on the grating smart window would show homogeneous when PEDOT is in bleach state.

Among of the possible materials that can be fabricated a grating, Al_2O_3 is of the most interesting. It has similar optical properties like the doped PEDOT. Filling in Al_2O_3 pores with PEDOT would enable us to have two dimensional grating; a tetragonal array grating. Rui Xiao has elaborated this possibility [11]. Another possible grating structure was proposed by R. Ganesan. It is fabricated the conventional line-pattern grating from Al_2O_3 through lithography technique [6]. Following this methodology, it is possible to construct the periodic of Al_2O_3 and PEDOT to form a grating.

It is utterly important to know which color or rather light spectrum should the grating smart window exhibit. Transmitted light spectrum from grating can be

calculated by using rigorous physics of optics and algebra. Gsolver is one of such examples. This program calculates grating problems by various numerical methods such as algebraic eigenvalue. The transmitted spectrum can eventually be transformed to the color via colorimetry, which corresponds to the human eye perception.

1.1 Objectives

We investigate the colors from grating smart window to find the feasibility to make the new type of smart window. The color can be evaluated from the spectral color that emerging from the grating smart window of PEDOT and Al_2O_3 when it under the sunlight source (D65). We use GSolver to simulate that spectrum and it also be transformed to color through colorimetry. This may help to find the appearance color on the grating smart window.

CHAPTER II

LITERATURE REVIEWS

This chapter describes the relevant underlying theories of the grating smart windows. First we describe the optical properties of constituents, PEDOT and Al₂O₃. Then, the optical theory about thin film and grating are explained. Cooperating with those theory and GSolver, the spectrum profile from the grating can be calculated. Changing that spectrum to color, it is required in order to perceive appearance color of the grating smart window.

2.1 PEDOT and Smart Window

2.1.1 Coloration of PEDOT

PEDOT coloration arises from the oxidation and reduction. The key is that when the PEDOT is doped by the ion, its color will change. The neutral state of PEDOT, or the reduced state has a deep blue color. When anion (An) is attached to PEDOT, it change to colorless (bleach state). This process can be considered as similar as electrolysis and can be depicted as



where An is an anion, which can recombine with Li⁺. Normally, lithium ion is chosen because of its small size which will result in reduction of the color changing time.

2.1.2 Structure for Electrochromic smart window

To achieve coloration process described in previous section, the electrochromic smart window is constructed from five different types of layers as shown in Figure 2.1. They are listed below.

1. Electrochromic Film: Material which reversible switch its color through the redox process. Its range is in nm- μm .

2. Electrolyte: A medium that allows the ions to move between ion storage and electrochromic layer. Its range is in mm [12], [13].

3. Ion Storage: This layer incorporates and releases the lithium ion used in the coloring process in electrochromic layer

4. Transparent Conductor: There are two parts for this type of layer. One is connected to the anode, and another one is connected to cathode. Its range is in nm.

5. Glass: There are also two layers of this type. They function as shields for the system and are ranged in cm.

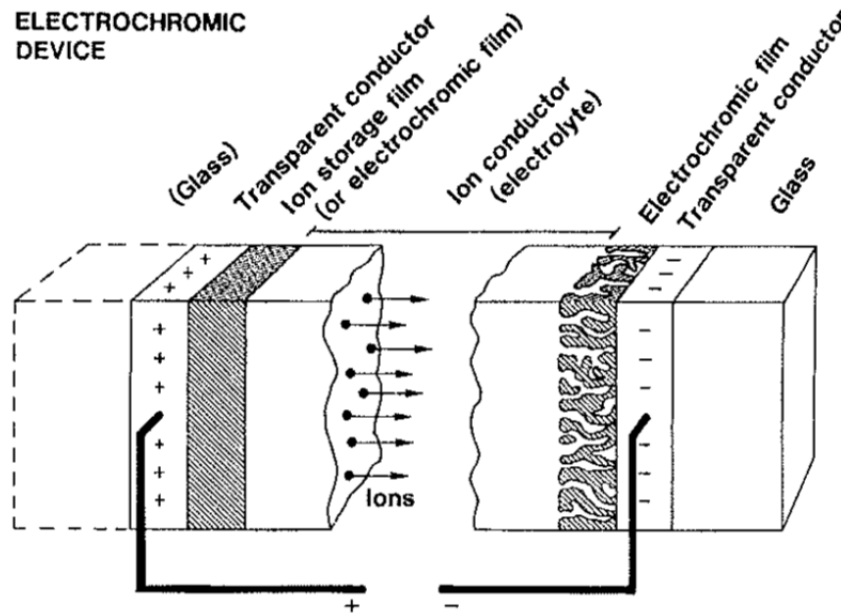


Figure 2.1 The layer of smart window device [14].

To control the direction of redox process in Eq. (2.1), two layers of electrodes are required. Controlling the movement of ions from ion storage to the electrochromic film is the function of transparent conductor layers. Normally, indium-tin-oxide (ITO) is used since it possesses high transparence and conductivity. Only thin layer of ITO is sufficient for the current to flow in the smart window [12].

Ion storage layer is meant to store ions, such as lithium ion, used in color changing process. The color of PEDOT is changed by redox reaction when the ions move through ion storage layer, electrolyte layer and PEDOT layer. One important property of the ion storage is that its optical properties remain the same when some

ions are added or removed from the layer. In some cases, PEDOT can act as the ion storage layer when used together with the tungsten trioxide. In the reduced state of tungsten, it appears bleach which corresponds to the oxidized state of PEDOT. When they are in the opposite state, they also appear the same deep blue color. Therefore, when PEDOT is used together with WO_3 in the smart window, it can switch between the bleach color and deep blue color. The blue color of that window will be darker than when only one of them is used because it has 2 absorbed layers.

Electrolyte is the ion solution which takes part in redox reaction. Its high conductivity will lead to more mechanically stable smart window. The ion conductivity is dominated by the ion movement. While the proton is the smallest ion, it cannot reverse back to hydrogen through the redox process. Consequently, the lithium ion is more appropriate. Moreover, lithium ion is more popular. Some of PEDOT smart window's recipes did not require the ion storage. The electrolyte, such as lithium tetrafluoroborate [15], can be connected directly to the transparent conductor of an anode side.

2.1.3 Selection of Conductive Polymers

Apart from PEDOT, there are many polymers that possess electrochromic property. Some of them have just two color states, and some have 3 color states as shown in Figure 2.3. For example, PEDOT and PEDOP have two states which is called doped (D) and neutral state (N), and the PEProDOP has three states of color. The additional color state appears during the changing between doped state and neutral state and is called intermediate state (I).

The conductive polymer that proper to smart window should hold ability in light controlling. The one that give high brightness different between neutral and doped state make the smart window become more worthy. The way to measure brightness should be measured respect to the human eyes. Intensity measurement at some specific wavelength may be a wrong idea. For example, the spectrum of transmitted light after propagate through an absorbed material, A and B are shown in Figure 2.2. At the wavelength 650nm, the transmittance from B is larger, but A also becomes larger when the wavelength is 400nm. It is equivocal and cannot specify whether A or B is more brightness. Hence, using some specific wavelength cannot

distinguish one from another. The better way for measurement is using the luminance which takes account of the whole light spectrum. It is the product from the transformation the spectrum to XYZ color index via colorimerty. The luminance is denoted by Y and it has unit in lumen. It corresponds to the brightness perception in human eyes. The detail of this will be explained in section 2.5.

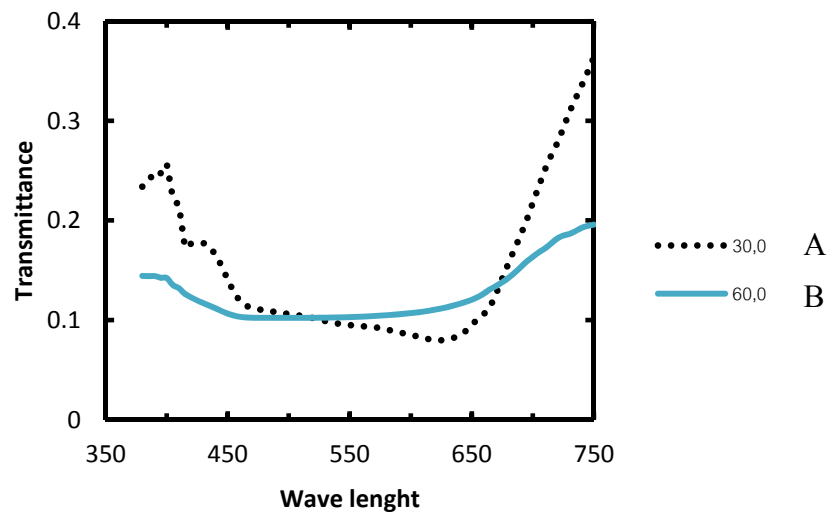


Figure 2.2 Transmittance spectrum from A and B material. It hard to tail which one is more brightness.

To compare luminance between doped and neutral state, we define the contrast in Eq. (2.2).

$$\text{Contrast} = 100 - \left(\frac{Y_{neutral}}{Y_{doped}} 100 \right) \tag{ 2.2 }$$

This quantity describe about the light controlling ability. If the contrast is very high, it means that the luminance between 2 states of that smart window is large and it is comfortable for smart window. For the most case, Y_{doped} is always larger than $Y_{neutral}$. Hence, the contrast value is in between 0 to 100.

A good smart window should give a high contrast. Barry [16] showed that only three conductive polymers that possess high contrast value than others. They are PEDOT, PProDOT-(CH₃)₂ and PEDOP which have a contrast 92.0, 80.8 and 79.2 respectively. From those values, it is reasonable to use the PEDOT as electrochromic

material in this study because it has the highest contrast value. Moreover, there are not much report about the others conductive polymer except PEDOT. Even though PProDop can give three colors instead two, but its performance is not impressive. All of PProDop states are rather same luminance, 51.7 in doped state, 49.9 in neutral state, and between these values is intermediate state. It mean that it has low contrast and not good for smart window.

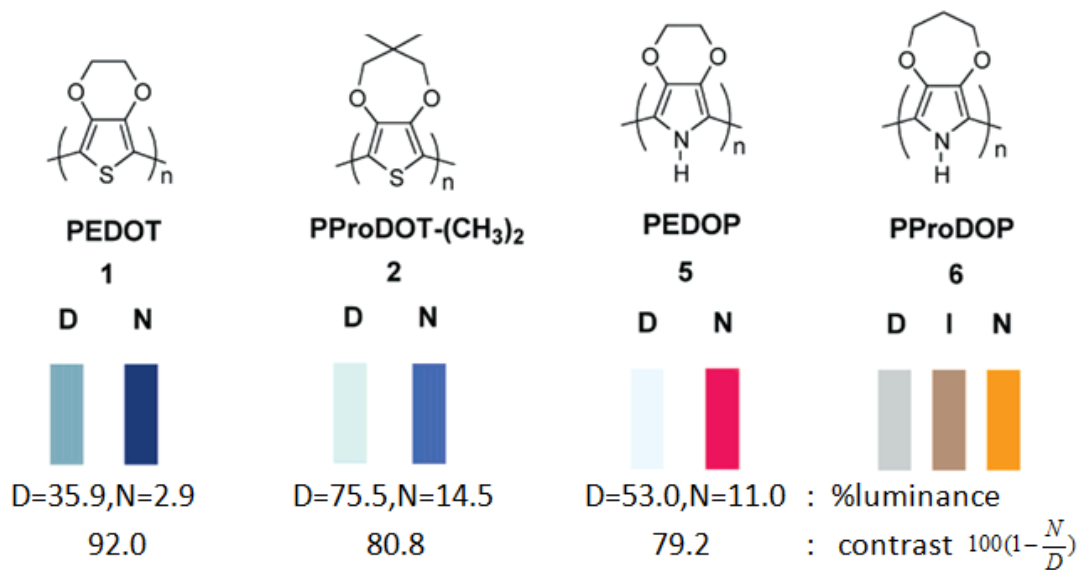


Figure 2.3 Depict the color, luminance and contrast both of doped state(D) and neutral state(N) of conductive polymer, i.e., PEDOT, PProDOT-(CH₃)₂, PEDOP and PProDOP [16].

2.1.4 PEDOT and WO₃

Finally, we compare the properties of the selected conductive polymer PEDOT with the current electrochromic material, the tungsten trioxide WO₃. The WO₃ is a good choice for the commercial because it is considered as the most successful electrochromic material. Many researchers are developing the method to optimize WO₃ for window devices. However, PEDOT may take place of WO₃ soon because of the following reasons.

- Contrast: Even though they are same color, but the light controlling ability of PEDOT is better than WO₃

- **Switching speed:** It should range in few seconds not minute. A smart window of tungsten oxide has a switching time around minute and depends primarily on its thickness [17]. Switching time of tungsten oxide can be reduced to 7-21 s by changing its physical structure to nanowire [18]. However, the switching time of PEDOT is in the order of millisecond [19]. Thus, PEDOT is much faster.

- **Long life time:** This is the most problematic for electrochromic material. In commercial desire PEDOT has a long life time, but its low cycle life stability is the major obstacle to their application [20]. It is expected to be longer in near future.

- **Flexibility:** It is another option, but it is required for the display application, PEDOT is basically flexible while tungsten lacks of this property [21].

From these desirable properties of electrochromic materials, PEDOT is a promising candidate over WO_3 . In addition, some laboratories notice that the oxidized state of tungsten oxide has a deep blue color while the PEDOT has the same color in a reduced state. Their color is also the same when they are in the opposite state, so it may be possible to apply PEDOT and tungsten trioxide together into a smart window because the reduction and oxidation are simultaneous reactions.

2.2 Diffraction Grating

Diffraction grating can split and diffract light into several beams, travelling in different directions. The grating is the periodic structure that constructs from different optical properties material such as open and opaque grating. This grating does not let some incident light propagate through as shown in Figure 2.4. The grating also can be made from two transparent materials which place in periodic and called phase grating or transmission grating as shown in Figure 2.5. The diffraction angle from those grating can be calculated from the same grating equation. From that equation, the direction of diffraction depends on period of grating, wavelength, incident angle and optical properties of surrounding materials. The grating equation cannot tell about the intensity of the diffracted light and it is rather complicated to calculate because it also depends on the thickness and the optical properties of the grating.

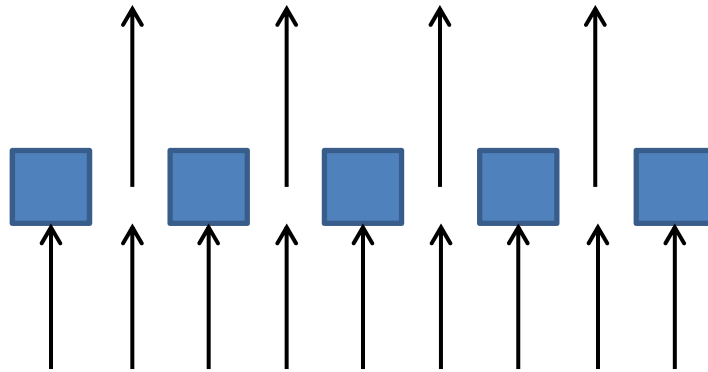


Figure 2.4 Open-Opaque grating. Some rays are obstructed.

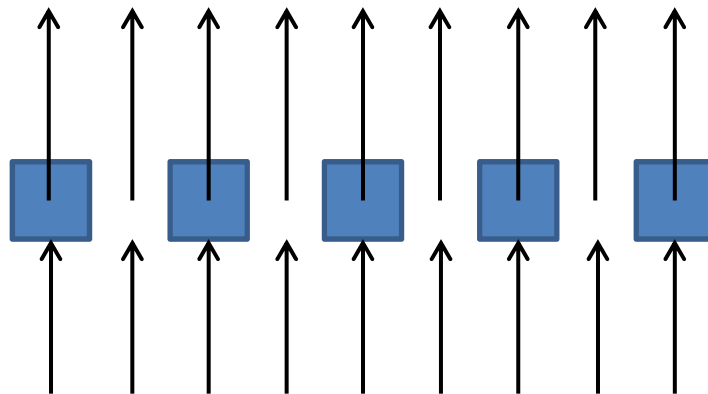


Figure 2.5 Transmission grating. All rays can propagate through.

By exploiting a grating structure to smart window, it may produce an art window like shown in Figure 2.6. It show various color because each wavelength (or color) is diffracted to different angle. It is the RVS transmission grating which is used with telescope to observe the distant galaxies, but when it is placed in a room that has white light, a mixed color can present on that RVS transmission grating [22]. Hence, addition grating structure to a smart window may give the art window like present by RVS grating.



Figure 2.6 RVS transmission grating under a white light from florescent bulb.

2.2.1 The Optical Properties of PEDOT and Al_2O_3

There are many materials that can be used to form grating structure such as SiO_2 , PMMA, Al_2O_3 . However, the one that had used with PEDOT is Al_2O_3 . The idea of grating smart window is its present various colors like Figure 2.6 when PEDOT is in neutral state and be like normal window when PEDOT is in doped state. If the complementary material that used to form grating structure with PEDOT has different optical properties to neutral state (dye), then the smart window may show the art color state. In contrast, if that material also has optical properties similar to doped state (transparent), then the window may like a transparent window. The optical properties that used for this propose are refractive index (n) and extinction coefficient (k). The n and k of Al_2O_3 , which illustrated in Figure 2.7, are collected from the GSolver database but it can compare to the SOPRA N&K (optical properties) database's Al_2O_3 [23]. For PEDOT, they are collected from by J. Hwang [24], and further explanation is given in chapter 3. In visible range (380-750nm), Al_2O_3 has zero value of k and has n around 1.66. Its k value is closer to the value of doped state than neutral state, n value also be such that. Therefore, it may proper to use Al_2O_3 with PEDOT to make grating smart window.

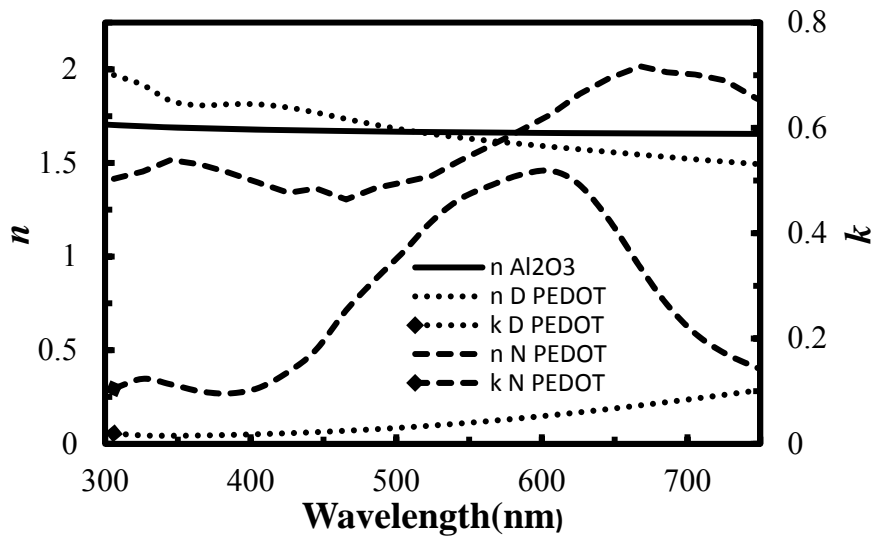


Figure 2.7 Refractive index (n) and extinction coefficient (k) of Al₂O₃ and PEDOT in neutral state and doped state in light spectrum.

2.3 The Light in Thin Film and Grating

To calculate the reflection and transmission intensity of any configurations, the one significant parameter is the optical path. It depends on the optical properties of the material that the light propagates through. It also depends on the propagation distance in material and from the angle. The optical path is used to find the constructive and destructive interference that relate to the diffraction.

2.3.1 Optical Constants

All materials are dispersive; the optical properties are wavelength-dependent. The optical properties are permittivity, dielectric constant, optical conductivity, absorption coefficient, refractive index and extinction coefficient, but all of these are not independent to each other. In physics, it prefers to use just the 2 of them that are refractive index (n) and extinction coefficient (k). They give the information about phase and damping of the light in matter respectively. The n and k are evaluated from the complex relative permittivity $\tilde{\epsilon}$. From application of Newton's second law to the electric force in matter and the assumption that the polarization of the matter has a vibration according to Hooke's law, it reveals that the permittivity is the function of the material natural frequency and plasma frequency. It also depends on the

frequency of the driving force or electric wave, so n and k also depend on that frequency. However, those frequencies is difficult to measure, therefore n and k are measure in another way. It relates to measure the intensity of reflection I_r , transmission I_t and the incident.

$$R = \frac{I_r}{I_0} = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2} \quad (2.3)$$

$$A = \log\left(\frac{I_0}{I_t}\right) = 2k_0 k z \quad (2.4)$$

R is a reflectance and A is an absorbance, k_0 or $2\pi/\lambda_0$ the wave number in vacuum and z mean the optical path length. The same symbol of k_0 and k can make some confusion. The first is a wave number while another is an extinction coefficient.

Sometime optical conductivity (σ) and absorption coefficient (α) also be used instead of n and k . The α can be written as a function of k by apply the Beer's law in Eq. (2.5).

$$I_A = I_0 \exp(-\alpha z) \quad (2.5)$$

substitute this I_A to Eq. (2.4), α become

$$\alpha = \frac{4\pi k}{\lambda_0} \quad (2.6)$$

We can use Eq. (2.3) and Eq. (2.6) to find α , but to find σ is more difficult. It is derived from the definition of permittivity in complex form ($\tilde{\epsilon}$). From the electromagnetic wave in matter, that complex permittivity can be written in formula:

$$\tilde{\epsilon} \equiv \epsilon_1 + \frac{4\pi i}{\omega} \sigma \quad (2.7)$$

To fine the refractive index, it need to give the definition first that is the ratio of wave velocity in vacuum (c) and matter (v_m)

$$n \equiv \frac{c}{v_m} \quad (2.8)$$

and if the material is nonmagnetic substance, the velocity is a function of permittivity:

$$v_m = \frac{1}{\sqrt{\epsilon}} \quad (2.9)$$

then n is a square root of permittivity or $n = \sqrt{\epsilon}$. If ϵ become complex, the refractive index then is a complex, that is

$$\tilde{n} = n + ik \quad (2.10)$$

after rearrange \tilde{n}^2 to set ϵ and compare the imaginary part with Eq. (2.7),

$$2kn = \frac{4\pi\sigma}{\omega} \quad (2.11)$$

substitute k with Eq. (2.6) and $\omega = 2\pi c/\lambda$ then σ :

$$\sigma = \frac{n\alpha c}{4\pi} \quad (2.12)$$

The equations of α and σ will be used in chapter 3 in order to change the optical properties database of PEDOT that reported in α and σ to n and k form. It needs to change for the simulation from GSolver.

2.3.2 Interference

Unlike the optical properties that is just a parameter, the interference is the important theory in optic which is the basis of all optical theory like thin film theory or diffraction theory. It occurs from the superposition between two or more electric wave. It isn't just the summation of the amplitude, but it also concerns the phase of the waves [25][26]. Consider the electric wave $\vec{E}_1, \vec{E}_2, \vec{E}_3, \dots$ gathering at some point, the producing of these is \vec{E} and called the superposition of wave

$$\vec{E} = \vec{E}_1 + \vec{E}_2 + \vec{E}_3 + \dots \quad (2.13)$$

For convenient, let assume that there are two wave, \vec{E}_1 and \vec{E}_2 or plane wave, propagate along the x axis in the same material

$$\vec{E}_1 = \vec{E}_{01} e^{i(kx - \omega t + \theta_1)}, \vec{E}_2 = \vec{E}_{02} e^{i(kx - \omega t + \theta_2)} \quad (2.14)$$

The phase term of the wave is the degree of exponential except i , and the scalar of \vec{E} is the amplitude of wave. Actually, the human's device can't measure the electric field, it can measure the irradiance (also known as the intensity) which given by

$$I = \epsilon v \langle \vec{E}^2 \rangle_T \quad (2.15)$$

$\langle \vec{E}^2 \rangle_T$ is the time average of the real part of electric field squared, or $\langle \vec{E} \cdot \vec{E} \rangle_T$ where T mean the time period of wave. Then the irradiance which produced from \vec{E}_1 and \vec{E}_2 is

$$I = \epsilon\nu\langle(\vec{E}_1 + \vec{E}_2) \cdot (\vec{E}_1 + \vec{E}_2)\rangle_T = \epsilon\nu\langle\vec{E}_1^2 + \vec{E}_2^2 + 2(\vec{E}_1 \cdot \vec{E}_2)\rangle_T \quad (2.16)$$

Let absent $\epsilon\nu$ for comfortable writing. The time average of some function is the integral over an interval T. Then

$$I = \langle\vec{E}_1^2\rangle_T + \langle\vec{E}_2^2\rangle_T + 2\langle\vec{E}_1 \cdot \vec{E}_2\rangle_T \quad (2.17)$$

or $I = I_1 + I_2 + I_{12}$, I_{12} is defined as the interference term. After taking the time average into account, each terms are

$$I_1 = \frac{E_{01}^2}{2}, I_2 = \frac{E_{02}^2}{2} \text{ and } I_{12} = E_{01}E_{02} \cos \delta \quad (2.18)$$

I_{12} can be written as a function of I_1 , I_2 , and δ which equal to $(\theta_1 - \theta_2)$ is the phase difference between these two wave. Then, the irradiance is

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos \delta \quad (2.19)$$

The maximum condition of the irradiance is obtained when $\cos \delta = 1$, therefore δ that equal $0, \pm 2\pi, \pm 4\pi, \dots$, can be called the constructive interference condition. The destructive interference will occur when $\cos \delta = 0$ or $\delta = \pm 1\pi, \pm 3\pi, \pm 5\pi \dots$. These conditions and the Eq. (2.19) are the base theory which can be applied to the light phenomena of thin film. In thin film optic, the phase difference δ will play the importance role to define which conditions give constructive or destructive interference.

2.3.3 The Reflection and Refraction at the Surface

When the electromagnetic wave impinges on a surface between two medium, it will be scattered. This result is come from the electron vibration of disturbance molecule, caused by the alternate electric field. Those will radiate the same frequency of electric field to all direction. It may be more ease if it is considered as a secondary point source. If that surface is smooth, flat surface, the directions of reflection and transmission will have just one direction because the scattered wavelets cancel the others in all direction except the exclusive direction where its phase is constructive. This non-evanescent direction is according to the law of reflection for reflected wave and law of Transmission or Snell's law for transmitted wave.

For the thin film theory, intensity of refraction and transmission wave are calculated from transmitted, reflected coefficients and the phase shift. The transmitted

and reflected coefficient are relate to the optical properties of the medium and the object which light propagated, while the phase shift is depend on the optical path length. More layers make the calculation more complicate. Besides, the theories that used to find those two in thin film theory are

1. The continuity condition state for the continuity of electric field at the surface or interface.

2. The law of refraction and transmission:

$$\theta_i = \theta_r$$

$$n_i \sin \theta_i = n_t \sin \theta_t$$

3. Faraday's law: $\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$

4. Irradiance (or intensity) equation: $I = \epsilon v \langle \vec{E}^2 \rangle_T$

With these, all the problem about homogeneous thin film can be solved as have written in many text book. However this book is not going to describe all formula from that far it just gives a simple idea to solve the problem with the formula.

Usually, the electromagnetic direction in matter is always described with two directions that are perpendicular to the plane of incident, and parallel to that plane. They are s-polarization p-polarization respectively. Therefore, any equation of the light in matter must concern the non-equality of the polarizations. For example, the reflected and transmitted coefficients light of electric field that propagate from medium i to medium t, are defined by

$$r_s = \frac{E_s^r}{E_s^i}, r_p = \frac{E_p^r}{E_p^i} \quad (2.20)$$

$$t_s = \frac{E_s^t}{E_s^i}, t_p = \frac{E_p^t}{E_p^i}$$

Superscript i, r, t mean incident, reflected and transmitted ray respectively and index s, p refer to polarizations. These values are always less or equal to 1. If the light fall on to with incident angle θ_i and propagate out with transmission angle θ_t , together with the continuity condition and Faraday's law, then each equation in Eq. (2.20) become

$$\begin{aligned}
 r_s &= \frac{n_i \cos\theta_i - n_t \cos\theta_t}{n_i \cos\theta_i + n_t \cos\theta_t} \\
 r_p &= \frac{n_t \cos\theta_i - n_i \cos\theta_t}{n_i \cos\theta_i + n_t \cos\theta_t} \\
 t_s &= \frac{2n_i \cos\theta_i}{n_i \cos\theta_i + n_t \cos\theta_t} \\
 t_p &= \frac{2n_i \cos\theta_i}{n_i \cos\theta_i + n_t \cos\theta_t}
 \end{aligned}
 \tag{2.21}$$

From Eq. (2.21), there is one special incident angle that is $\theta_i = 0$. At this angle, there is no different between s and p polarization because $r_s = r_p$ and $t_s = t_p$.

The equations from Eq. (2.20) to Eq. (2.21) are the case for light incident just one interface. For the case of double surface, as shown in Figure 2.8, or a single thin film, the light propagate through two interfaces and the calculation become more complicated. The coefficients can be calculated by the superposition of the ray that reflected (ray 1, 2, 3 in Figure 2.8) or transmitted (ray 5, 6) in parallel direction which given by

$$\begin{aligned}
 r_s &= \text{Re} \left[\frac{r_{1s} + r_{2s} e^{-i\delta}}{1 + r_{1s} r_{2s} e^{-i\delta}} \right] \\
 r_p &= \text{Re} \left[\frac{r_{1p} + r_{2p} e^{-i\delta}}{1 + r_{1p} r_{2p} e^{-i\delta}} \right] \\
 t_s &= \text{Re} \left[\frac{t_{1s} t_{2s} e^{-i\delta/2}}{1 + r_{1s} r_{2s} e^{-i\delta/2}} \right] \\
 t_p &= \text{Re} \left[\frac{t_{1p} t_{2p} e^{-i\delta/2}}{1 + r_{1s} r_{2s} e^{-i\delta/2}} \right]
 \end{aligned}
 \tag{2.22}$$

Subscript 1 and 2 refer to the first and second interface that light propagate through, δ is the phase different between the ray that come along with that direction like phase different of ray 1 and 2 in Figure 2.8. Usually, δ is $2k_0 n_f d \cos\theta_i$ where d is the film thickness but it also may be added with phase shift π if $n_i < n_f > n_t$ or $n_i > n_f < n_t$ the coefficients in Eq. (2.22) can be calculated like Eq. (2.19), for example r_{1s} is calculated from material n_i and n_f as shown in Figure 2.9.

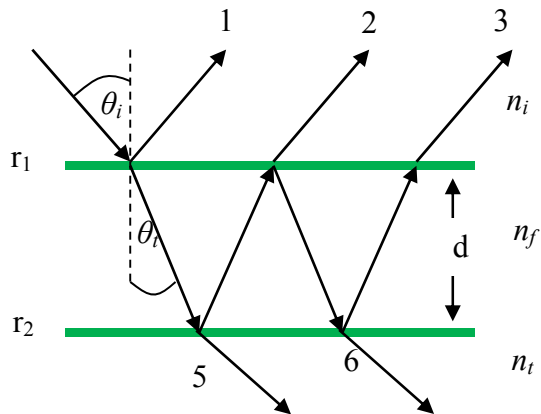


Figure 2.8 Light propagation through single thin film, where n_f is film refractive index and surrounded by material with the refractive index n_i and n_t , d is film thickness.

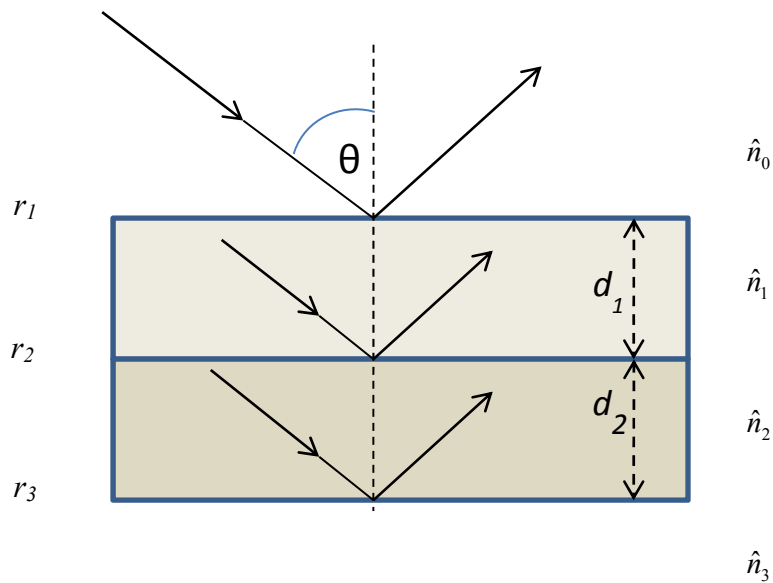


Figure 2.9 Double layer thin film which thickness d_1 and d_2 surrounded by materials that have refractive index \hat{n}_0 and \hat{n}_3 .

In this study, we assumed that the grating layer is just a thin film layer, and then it can be approximate to the double layer of thin film (Figure 2.9). From the fact that some of our materials have extinction coefficient, then the refractive index is treated as complex value, for example $\hat{n}_1 = n_1 + ik_1$. It is more complicated than the single layer, but it uses the same idea. If the incident angle is zero, then $r_s = r_p$ and it can be written that

$$r = \frac{r_1 + \overline{r_2} e^{-i\delta_1}}{1 + r_1 \overline{r_2} e^{-i\delta_1}} \quad \text{when} \quad \overline{r_2} = \frac{r_2 + r_3 e^{-i\delta_2}}{1 + r_2 r_3 e^{-i\delta_2}} \quad (2.23)$$

or

$$r = \frac{r_1 + \frac{r_2 + r_3 e^{-i\delta_2}}{1 + r_2 r_3 e^{-i\delta_2}} e^{-i\delta_1}}{1 + r_1 \frac{r_2 + r_3 e^{-i\delta_2}}{1 + r_2 r_3 e^{-i\delta_2}} e^{-i\delta_1}} \quad (2.24)$$

which can be rewritten as

$$r = \frac{r_1 + r_2 e^{-i\delta_1} + r_3 e^{-i(\delta_1 - \delta_2)} + r_1 r_2 r_3 e^{-i\delta_2}}{1 + r_1 r_2 e^{-i\delta_1} + r_1 r_3 e^{-i(\delta_1 - \delta_2)} + r_2 r_3 e^{-i\delta_2}} \quad (2.25)$$

In our study, some of our materials have complex refractive index, so r_1 , r_2 and r_3 in Eq. (2.25) is a complex number.

$$r_1 = \frac{\hat{n}_0 - \hat{n}_1}{\hat{n}_0 + \hat{n}_1}, \quad r_2 = \frac{\hat{n}_1 - \hat{n}_2}{\hat{n}_1 + \hat{n}_2}, \quad r_3 = \frac{\hat{n}_2 - \hat{n}_3}{\hat{n}_2 + \hat{n}_3} \quad (2.26)$$

The complex number Eq. (2.26) will be more convenient to Eq. (2.25) if it change to exponential function by using Euler's formula.

$$r_1 = |r_1| e^{i\beta_1} \quad (2.27)$$

$$\text{when } |r_1|^2 = \frac{(n_0 - n_1)^2 + (k_0 - k_1)^2}{(n_0 + n_1)^2 + (k_0 + k_1)^2} \quad \text{and} \quad \beta_1 = \tan^{-1}\left(\frac{k_0 - k_1}{n_0 - n_1}\right) - \tan^{-1}\left(\frac{k_0 + k_1}{n_0 + n_1}\right) \quad (2.28)$$

The others, r_2 and r_3 , are just like r_1 . Then the phase different δ_1 and δ_2 are complex, and they can be written as

$$\delta_1 = \delta_{1R} + \delta_{1I} = 2k_0 n_1 d_1 + i2k_0 k_1 d_1 \quad (2.29)$$

$$\delta_2 = \delta_{2R} + \delta_{2I} = 2k_0 n_2 d_2 + i2k_0 k_2 d_2 + \pi$$

where k_0 is the wavenumber in vacuum. The phase shift π need to add to δ_2 because the real part of our material is $n_1 < n_2 < n_3 > n_4$. Accordingly, the coefficient r in Eq. (2.25) is

$$r = \frac{|r_1| e^{i\beta_1} + |r_2| e^{-\delta_{1I}} e^{i(\beta_2 - \delta_{1R})} + |r_3| e^{-(\delta_{1I} + \delta_{1I})} e^{i(\beta_3 - \delta_{1R} - \delta_{2R})} + |r_1| |r_2| |r_3| e^{-\delta_{2I}} e^{i(\beta_1 + \beta_2 + \beta_3 - \delta_2)}}{1 + |r_1| |r_2| e^{-\delta_{1I}} e^{i(\beta_1 + \beta_2 - \delta_{1R})} + |r_1| |r_3| e^{-(\delta_{1I} + \delta_{2I})} e^{i(\beta_1 + \beta_3 - \delta_{1R} - \delta_{2R})} + |r_2| |r_3| e^{-\delta_{2I}} e^{i(\beta_1 + \beta_2 + \beta_3 - \delta_{12})}} \quad (2.30)$$

and the reflectance or R is equal r^2 .

2.3.4 The Dispersion of Light by a Grating

Grating is the periodic structure which acknowledged as the device to disperse or diffract the light. The famous theory that used to describe this phenomena is the Huygen's Principle, which state that *every unobstructed point of a wave front, at a given instant, serves as a source of spherical secondary wavelets* [25]. It is extremely suitable to describe the diffraction from open-opaque grating, each transparent channel act as a secondary point source (Figure 2.10). Each of them generate the electric field $E(r)e^{i(kr-\omega t)}$

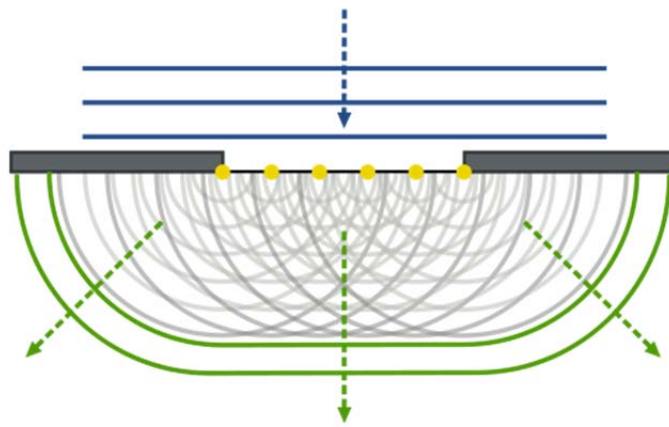


Figure 2.10 Secondary point source on an aperture [27].

If the grating has periodic in x direction, the intensity of the integral to the wavelet of secondary point source (denote by white in Figure 2.11) along the x axis, sum over each channel and change the electric field to the intensity; it will give equation:

$$I = \frac{I_0}{N^2} \left(\frac{\sin \beta}{\beta} \right)^2 \left(\frac{\sin N\alpha}{\sin \alpha} \right)^2 \quad (2.31)$$

Where $\beta = \frac{kb}{2} \sin \theta$ and $\alpha = \frac{ka}{2} \sin \theta$, N is number of secondary point source in one channel, a is the period of grating, b is the width of groove, and k is wave number. The graph of Eq. (2.31) also be plotted along α when $\alpha = 2\beta$ and $N = 6$ like shown in Figure 2.12.

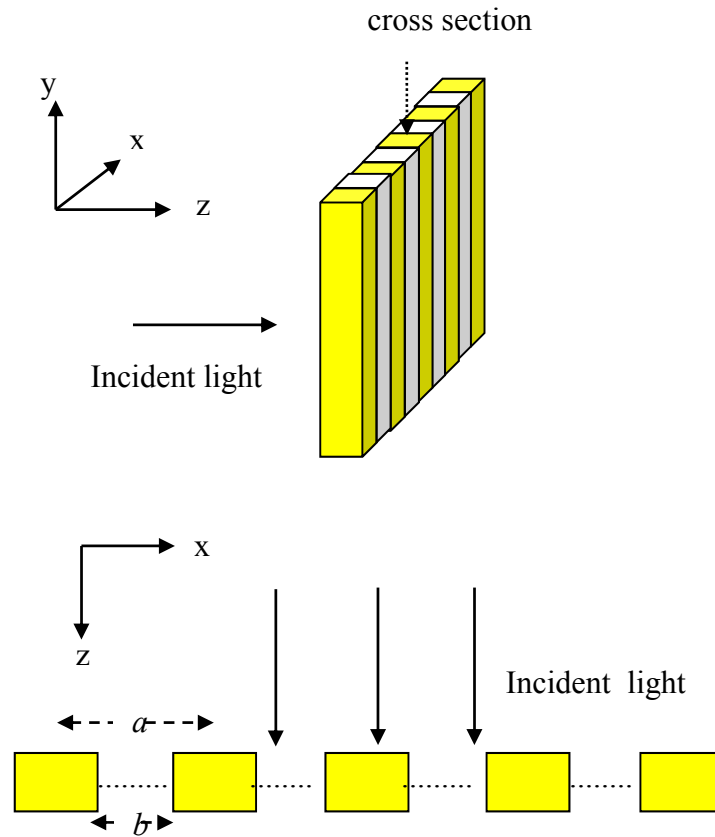


Figure 2.11 Cross section of grating, a as a period and b as a width of grating.

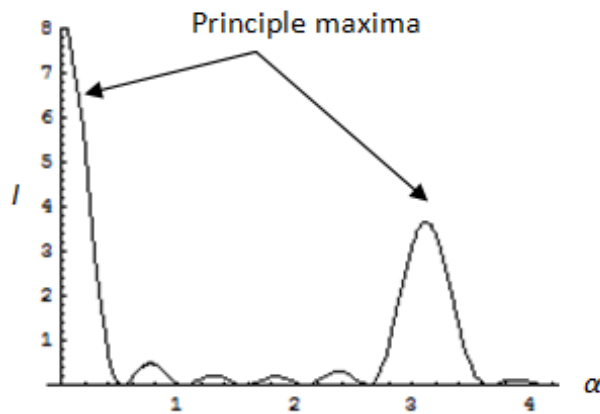


Figure 2.12 Multiple slit pattern, $I = \left(\frac{\sin\beta}{\beta}\right)^2 \left(\frac{\sin N\alpha}{\sin\alpha}\right)^2$ when $\alpha = 2\beta$, $N = 6$.

The peak that called principle maxima occur when $\sin\alpha$ equal 0, so α is the number that number multiplied with π , $0, \pm\pi, \pm2\pi, \dots$. It can be written in a formula as

$$\frac{ka}{2} \sin \theta = m\pi \quad \text{where } m = 0, \pm 1, \pm 2, \dots \quad (2.32)$$

Or $a \sin \theta = m\pi$ if the surrounding materials are vacuum and the incident angle is zero. This is the famous equation, called grating equation. Even though there are small peaks that called principle minima but its intensity is much weaker than that of the principle maxima. Hence, the principle minima is ignored in our simulation

There is grating that not has an opaque material like the previous, but it is the periodic from two different transparent materials. It is called transmission phase grating [28] which quite ambiguous to apply the Huygen's Principle because each point on grating can act as secondary point source. If we assume that it can work like the previous cause which calculate just the point source in open channel along x axis, but now, the point on two transparent materials also included. The point source inside the grating may affect the wavelet of the surface point source, so the integral may be take along 2 direction, x and z axis and it may become gross. The physicist doesn't calculate this problem using Huygen's principle, but it can be solved by solution from pseudo periodic field [29].

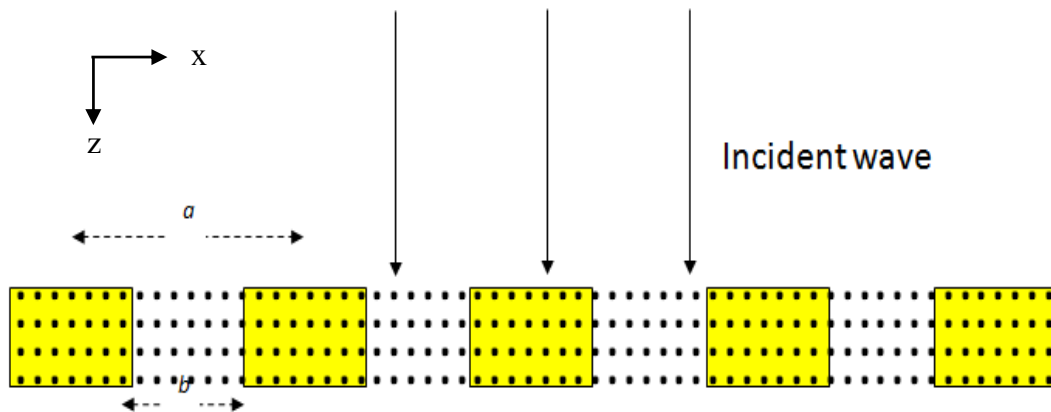


Figure 2.13 A secondary point source for a transparent phase grating.

The pseudo-periodic field will be discussed briefly. It assume that the periodic grating cause the amplitude of the diffracted wave be periodic. If the light travel in plan xz with the incident angle θ and grating is periodic in x, then the pseudo-periodic field can be written as

$$E^d(x+d, z) = E^d(x, z)e^{ik_0 d \sin \theta} \quad (2.33)$$

By using total field equation for periodic grating along x and y axis, Fourier series (to write equation of periodic) and Helmholtz equation (wave equation for electromagnetic wave), the grating equation for diffracted waves both reflected and transmitted of arbitrary grating 2dimensional grating along x and y axis will be written as

$$\begin{aligned} k_d \sin(\theta_{d,m}) \cos(\phi_{d,m}) &= k_i \sin(\theta_i) \cos(\phi_i) + \frac{2\pi m}{d_x} \\ k_d \sin(\theta_{d,m}) \sin(\phi_{d,m}) &= k_d \sin(\theta_i) \sin(\phi_i) + \frac{2\pi m}{d_y} \end{aligned} \quad (2.34)$$

The angles are described by two parameters, θ and ϕ to cover angles in three dimensions. θ_i, ϕ_i are the incident angle, $(\theta_{d,m}, \phi_{d,m})$ mean the diffracted angle of the m order of diffraction, both reflected and transmitted ray. k_i is wave number for incident side but k_d is wave number which reflected or transmitted ray. Just like previous grating equation, these conditions stand for principle maxima or non-evanescent wave. The grating equation from Huygen's Principle can determine only one angle or it cover the light that travel in a plane, but the new grating equations cover the light in three dimensions. It also cover two dimensional grating that have periodicity in x and y axis. To use Eq. (2.34) for one dimensional grating as our study, in such case, the grating is periodic in x direction and no longer have period in y direction, then $d_y \rightarrow \infty$ and term $2\pi m/d_y$ is vanished. This grating equation just gives about the diffracted angle and not concern the optical properties of the grating. The optical properties for this equation are just surrounding materials, so if that equation also held for the grating that coated by thin film.

There are some special cases of grating that called Grating waveguide structure which very similar to our structure, it has a transparent grating layer and a transparent wave guide layer. It gives an anomalous peak in very strict condition, and it can make the transmittance or reflectance reach the extreme value, some case have reach to 0 or 1. Calculation the position of peak through GSolver can compare to the real, if the conditions are the same. It will be explained later in appendix A.

2.3.5 The sunlight

The sunlight should be accounted to our configuration because the smart window is surrounded by sunlight in general. The worse properties of sunlight are short coherent and unpolarized light. They can destroy the interference from grating and thin film, but there are some limits conditions of grating that may make diffraction remain under the sunlight.

Coherent length is important to the thin film theory. It describes the length of wave continuity, and it allows us to predict the phase of the wave at a given point. For example, the superposition from two wave, one is known its phase, but the other is not, then the result of this superposition become problem because the phase different is unknown, and it makes the intensity equation, Eq. (2.19), cannot be calculated. It also affects the thin film theory since the phase different is important to calculation. For example, to calculate the reflectance, it uses the ray number 1,2,3 and further in Figure 2.8, the optical path length of them in reflecting angle θ_i are different by $2dn_f \cos\theta_i$. This value can be used to predict the constructive interference or destructive interference, both of reflectance and transmittance, and it is helpful for thin film technology. If the light has coherent length shorter than that value, that prediction may become wrong or less effective. For this reason, the coherent length is very important to thin film theory.

The diffraction from grating also has a problem with short coherent light. In one dimensional grating problem likes Figure 2.14 with an approximately way, the path different of ray 1,2,3 are used to calculate the condition of constructive interference and destructive interference. Unlike the thin film, the optical path different of each ray is different by $n_t a \sin \theta_t - n_i a \sin \theta_i$, but if the coherent length lower than this value, the interference prediction may become wrong or less effective.

There has been a report of sunlight coherent length in vacuum; it is about $0.6\mu\text{m}$ [30]. This value is lower than DVD and CD gab period, those grating period are $0.72\mu\text{m}$ and $1.52\mu\text{m}$ respectively. However, the rainbow tab or diffraction pattern appears on DVD and CD under the sunlight even though the period is longer than that coherent. The pattern of DVD and CD are different; the color pattern on DVD seem to sharper than CD. It may think that the DVD which has period close to sunlight coherent length seems to have complete interference more than CD. Hence, it can be

assumed that the shorter grating period can present the sharper color in color pattern even though the period is longer than the coherent length of impinging light.

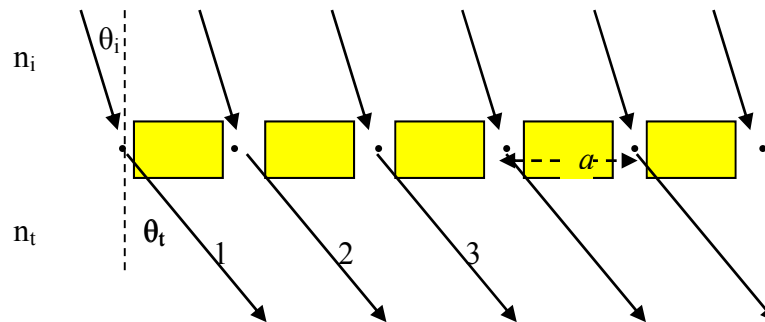


Figure 2.14 Light propagate through normal grating, where n_i is refractive index of incident side and n_t is refractive index of transmit side.

2.4 Trail of the Color Representation on Grating

We already have known that there are various colors on grating. We could calculate the diffraction angle of monochromatic light from grating but we lack the way to represent that color. For instance, what color is that when the light is just 690nm? It is red, hard red or orange? And the problem are complicating if there are many of monochromatic wave like spectrum. Imagine that we have grating and it exposed by the same intensity of light from all direction. According to the grating equation, there must have many monochromatic lights that diffracted to that same point after grating. It seem hopeless if we mixed many light colors without apply some theory. Fortunately, the ways to find the color have developed long time ago, since the effort to distinguish and classify the color. A system for categorizing colors called "Color order system". It has 3 major categories, but the one that appropriate to this study is a pure physical approach, which consists of the CIE RGB and CIE XYZ system (CIE is a contract form of International Commission on Illumination). It base on human perception and the way to convert the spectrum to color like is illustrated in Figure 2.15. It is called colorimetry or transform a spectrum to the color index (XYZ), and it can transform to the form that acknowledged by a computer (RGB). Consequently, we can represent the color on our grating.

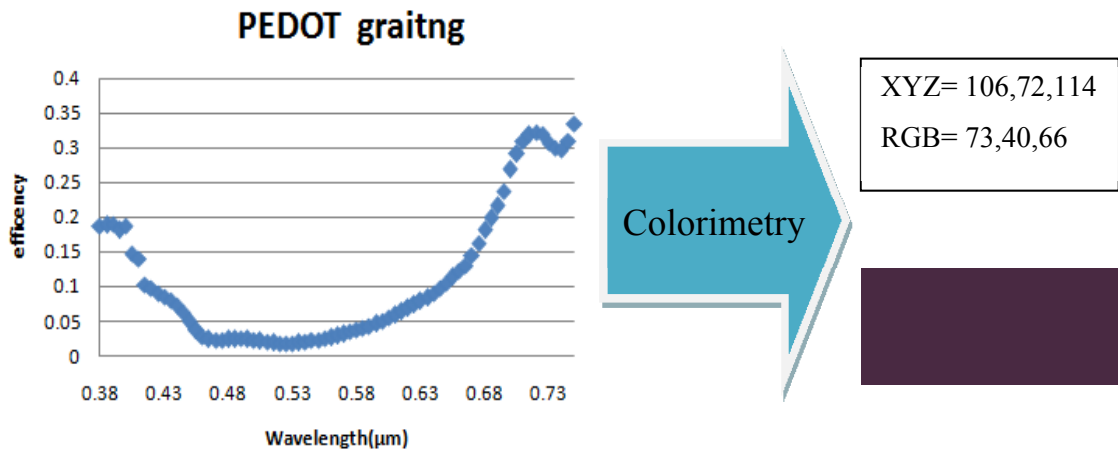


Figure 2.15 Color of the PEDOT calculated from spectrum.

2.5 Color Order System and Colorimetry

Color order system is a system for categorize colors [31]. There are many established system such as Munsell, which established since 1981 and still be used. This system uses 3 parameter of hue (tone color), value, and chroma (white sensation). Munsell system does not related to the incoming spectrum into the eyes, so it is not suitable to our study. There is another color system that base on the photo-respond to the spectrum. The human photoreceptions consist of 3 types of cone cell and 1 rod cell. These 4 signals from each receptor are reduced to 3 signals by nerve system, called Opponent Process [32]. That may be the reason why the colors, such as RGB or XYZ, need just 3 parameters for description.

The famous color order system that quite universal is CIE RGB and CIE XYZ. Those color systems use the superposition of three primary colors or color matching functions that is described in Figure 2.16- Figure 2.17, which have different spectrum curve. The components of each primary color are called tristimulus value, and the color indexes of the spectrum depend on how much each primary color responds to that spectrum. Those three combinations can also match the color from a monochromatic light source. In the other hand, if we can have the sources that can emit the primary color spectrum, it will represent all human perception colors. This is contrast to the RGB system that was derived since 1920, some of them have negative

value and it is impossible to build the source like that. Consequently, the other derived system need to be without negative value that is the XYZ.

It should be noted that RGB system and the color index RGB, which used in now a day such as sRGB or Adobe RGB, are different. It is because the name of the later one is founded from the real light sources that emit red, blue and green color, while the RGB system is use the imaginary light sources.

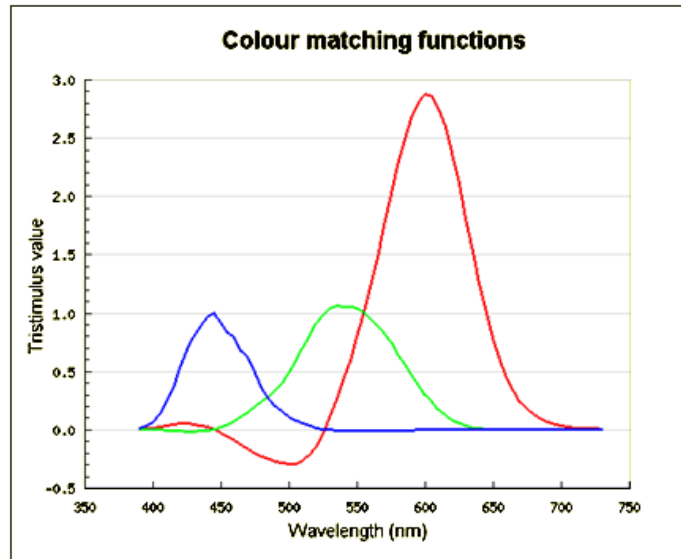


Figure 2.16 RGB color matching functions [33].

Later, in 1931, new primary colors with non-negative value were established with a full name *Color Matching Functions for the Standard Colorimetric Observer*. In short in called CIE 1931 XYZ (but let call CIE XYZ) and the thristimulus values are denoted by X, Y and Z and defined by

$$\begin{aligned}
 X &= K_m \int f(\lambda) \bar{x}(\lambda) d\lambda \\
 Y &= K_m \int f(\lambda) \bar{y}(\lambda) d\lambda \\
 Z &= K_m \int f(\lambda) \bar{z}(\lambda) d\lambda
 \end{aligned}
 \tag{2.35}$$

$\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ are the color matching functions which official reported by CIE Technical Committee [13], [34] and represented in Figure 2.17, which have unit less. The integral take to the incoming spectrum $f(\lambda)$ over the light spectrum (in our study,

we chose from 380 to 750nm). The spectrum $f(\lambda)$ is the intensity superposition from monochromatic then it should have a unit in radiant flux per unit wavelength. The constant K_m is 683 lm/watt. Hence, a unit of X, Y and Z are lm or lumen. It is rather specific for $\bar{y}(\lambda)$ which particularly designed to match with the CIE photonic luminous efficiency function($V(\lambda)$) then Y value is proportional to the luminous or luminance of the object, while the value of Z is correspond to blue, and X is mixed between red and blue as shown in Figure 2.17. Those primaries also are derived to have same area; such property can be written as

$$\int \bar{x}(\lambda)d\lambda = \int \bar{y}(\lambda)d\lambda = \int \bar{z}(\lambda)d\lambda \quad (2.36)$$

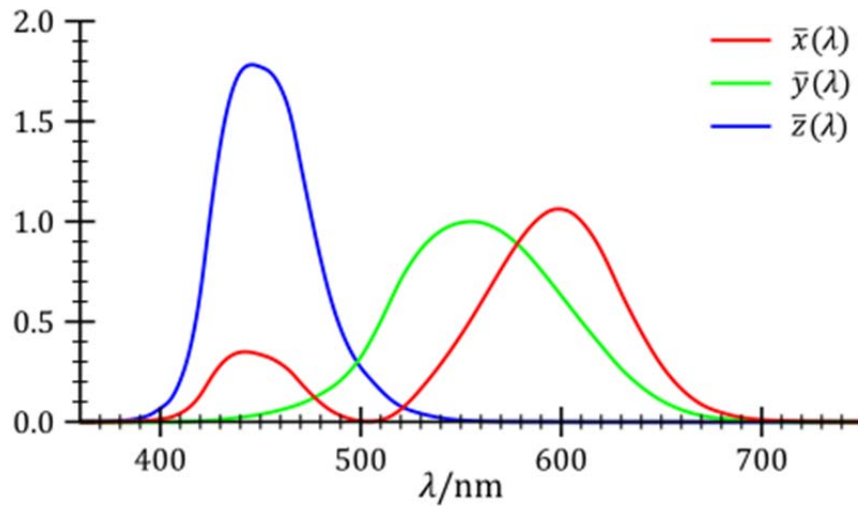


Figure 2.17 CIE XYZ color matching functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ [13].

There is another form of XYZ to describe the object's color. It consist three parameters as previous, one of them will represent luminance while two left will tell about tone color. The luminance has already defined, it is Y value, while the color tone is defined from x, y and z:

$$x = \frac{X}{X + Y + Z}, y = \frac{Y}{X + Y + Z}, z = \frac{Z}{X + Y + Z} \quad (2.37)$$

The properties of xyz are

$$x + y + z = 1 \quad (2.38)$$

and when $x = y = z = 1/3$, it will represent the pure white color. Those cannot go to negative value since the XYZ cannot be negative. It is reasonable to use just x and y

since z can be found through Eq. (2.38). Hence, all color tone of the object can be plotted in two dimensional spaces (xy space as shown in Figure 2.18) and we called that value as chromaticity (color of object without luminance or brightness). However, just two degree of freedom of xy chromaticity value is not a real color of the object because lacking brightness, but with addition Y to be Yxy will cover the real color and it can transform back to XYZ . The separate description of the brightness and the chromaticity is a good point of Yxy index.

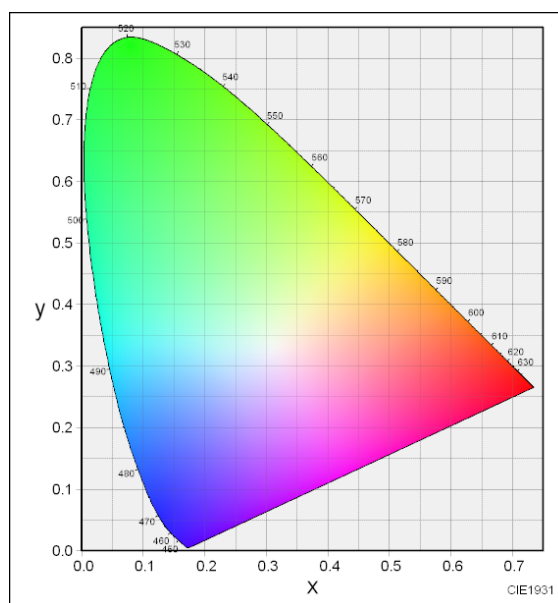


Figure 2.18 The xy color space, describing the chromaticity of the object.

Even though the human can find the all color they can see, but it a limit to their device for displaying all color [35] if it not the primary colors. We can't reach some colors by our device, for example by painting, printing or displaying. The color space that can represent by a device is called gamut (Figure 2.19) which dependent on the physical characteristic of that device. Normally the color space that apply in a commercial LCD is sRGB and for high end is AdobeRGB 1998(larger gamut). A normal printer can represent color in CMYK color space and hexachrome (CMYKOG). Note that, the primaries of sRGB and AdobeRGB are not the primaries of RGB as described before, but they correspond to the light sources of red, green and blue in the LCD or CRT monitor. To represent color between the display system and printer system, they need to be transformed to XYZ first and then be transformed to

the color index of the destination device. This is according to the discipline of the International Commission on Illumination. Some problems of color representation can arise between the LCD and printer. It because the boundary of gamut for the LCD display and the printer are not the same as shown in Figure 2.19, some color can display by LCD but the printer can't produce that color. This can be solved through some approximations that make the out of gamut color move to inside gamut but it also disturb all color of the picture. However, this approximated color may not make normal people be annoying except for the expert of color like a photographer. Note that, the color space in Figure 2.18 and Figure 2.19 are an approximated color because the fact that there is not device that can represent all colors.

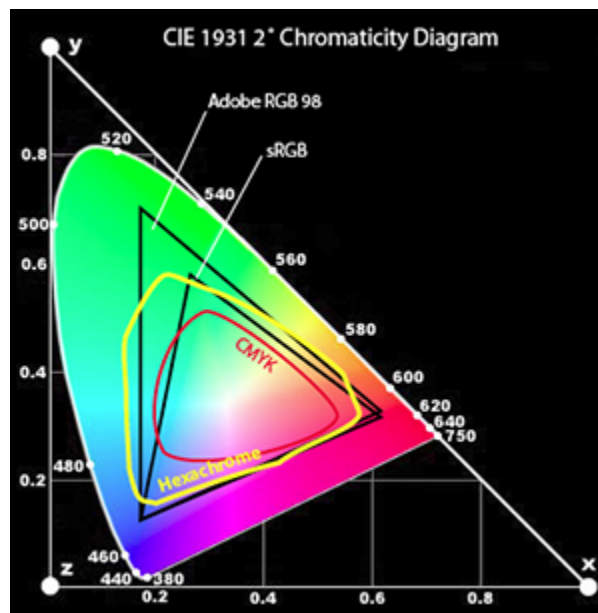


Figure 2.19 Gamut regions show the color space for sRGB, Adobe RGB, CMYK and hexachrome [35].

There are two CIE standard observer that is CIE 1931(2°) and CIE 1964(10°), 2° and 10° are the observation angle. These two have different matching function (but different a little). Some paper recommended using CIE 1964(10°) for observing the homogeneous sheet, but in this study, the grating has various colors depend on the observation angle. Using the color matching for homogeneous may not proper to the grating's color. So it may be appropriate to choose CIE 1931(2°) for the matching functions.

2.6 Encoding from XYZ to sRGB

This work is going to find the color from grating. After calculation the spectrum at any point and changed to color index XYZ, then it need to transform to sRGB color space for LCD representation. To avoid the difficult of the transformation, it is easier to use the white light as the sRGB white source (called white point) and fortunately it is D65 or the daylight color at the noon in Europe [13]. It is more difficult if we study under the lamp, orange light; it require the some method that will help to get rid of the orange color and it quite complicate. The XYZ from D65 need to be normalized by apply the coefficient that make the Y equal 1.000, and it will make $X = 0.9504$ and $Z = 1.089$ automatically. Now, after the light from D65 diffracted by grating and be changed to XYZ, it can be transformed to the sRGB color space through the matrix operation.

$$\begin{bmatrix} R_s \\ G_s \\ B_s \end{bmatrix} = \begin{bmatrix} 3.2406 & -1.5372 & -0.4986 \\ -0.9689 & 1.8758 & 0.0415 \\ 0.0557 & -0.2040 & 1.0570 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} \quad (2.39)$$

The color component transfer function is as below:

$$R = R_s * 12.92, \quad G = G_s * 12.92, \quad B = B_s * 12.92 \quad (2.40)$$

If R_s , G_s or B_s are greater than 0.0031308

$$\begin{aligned} R &= 1.055 * (R_s)^{1/2.5} - 0.055 \\ G &= 1.055 * (G_s)^{1/2.5} - 0.055 \\ B &= 1.055 * (B_s)^{1/2.5} - 0.055 \end{aligned} \quad (2.41)$$

This is the encoding profile from International Color Consortium or ICC for the sRGB (Document: IEC 61966-2-1:1999). This RGB is in range 0-1. It is possible that some values exceed 1 or can be negative. That value is come from the color that out of sRGB gamut, for example $x, y = (0.5, 0.2)$ as shown in Figure 2.19. It is no exact way to deal with that problem color, we can approximate that color in many ways. Finding the closest point to sRGB is the method that we use for such a problematic color.

CHAPTER III

PREPARATION AND METHODS

This thesis simulates spectra from grating smart window and converts it to color. We interest three grating type; some of them can be fabricated. Spectra from those grating are simulated by GSolver. However, the optical properties of PEDOT are not in the GSolver database, so it is requirement in order to simulate spectra. We investigate the spectrum from all angles, so it needs to explain our configuration. Those spectra will be transformed to XYZ or Yxy color index via colorimetry. To describe what color on grating, we draw the field of view which represents the color in two dimensions. The position of field of view relate to the transmitted angle of the light from the grating smart window.

3.1 Grating Structure

The grating structure that used for this study consists of electrochromic layer and ITO layer because these layers are small enough that the interference from the sunlight can occur. Therefore, the calculation will use just those layers to find the spectrum. Three types of gratings are used in this study (Figure 3.1), the grating layer is 1-dimensional periodic of PEDOT and Al_2O_3 . Each of them is quite familiar to each other but for a grating, a little different structure is enough to produce a different interference. It means that the color from these three grating may be different. The first grating, structure A, is similarly designed and fabricated by Ganesas et al. [6] or a single line grating of PEDOT and Al_2O_3 . Structure B is just like A, but added the bottom layer to ITO to form a double grating layer. This additional layer is similar to the top layer and those PEDOT of the top and the bottom coincide to each another. Structure C is just like structure B, but the coinciding of the top and bottom layer is PEDOT and Al_2O_3 . Structures B and C give more surface area than structure A when PEDOT volume of A, B and C structures are equal. The larger surface produces faster

switching time like occur in the nanorod PEDOT [36]. It is similar to B and C structures,

Normally, above of the grating layer is the electrolyte solution, while underneath the ITO layer is glass. Both of those will be treated as superstrate and substrate, respectively. Those refractive indices are also used in calculation, and those are not much disperse in light spectrum, so they and can be treated as constant refractive index with 1.33 and 1.50 for the electrolyte and glass respectively. This thing will apply to structure A, but for structures B and C, the substrate and superstrate are the electrolyte solution.

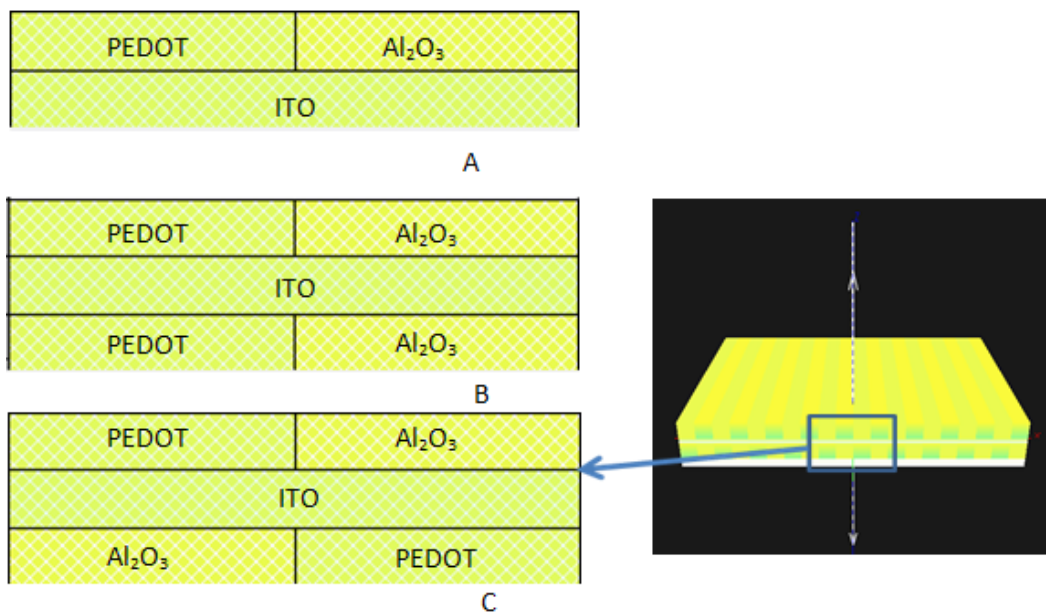


Figure 3.1 Cross section of A, B and C grating structures.

There are three parameters of grating structure that can be modified. These are period of grating and thickness of grating layer and ITO layer. Those length are limited because of the sunlight coherent length, those value should be lower than 720nm (from the DVD period that still occur the diffraction under the sunlight). The grating period should be larger than 380nm, the diffraction from grating will not occur if the period is lower than that value; it is the minimum limit of the period. Therefore, the grating period can be anything in that limit, and 550nm is an interested period our structure. Similarly, the constructive and destructive from the thin film would not

occur if the optical path different is lower than that value. Therefore, the thickness should be smaller as possible and we select 350nm and 100nm are the thickness of grating layer and ITO layer respectively.

3.2 GSolver

GSolver program is used in order to find the transmission spectrum from grating. It give numerical solution from Maxwell's equation for periodic grating structure that surrounded by 2 homogeneous materials, substrate and superstrate. The light intensity of each direction is obtained through Algebraic Eigenvalue model which is the most recommend model by the program. Any grating structure can be simulated from any material by the program, for example, a blazed grating. Some material profile does not exist in the program database, but it can be added later such as PEDOT. GSolver also provide the calculation in wavelength, but it should be match with the material profile. For example, the calculation about Al_2O_3 must be in range of its optical properties dispersion in GSolver database that is between 250-926nm. This study use light spectrum or wavelength between 380 to 750nm (step every 5nm), so Al_2O_3 is not a problem for this calculation, ITO does too (normally this GSolver contain the refractive index dispersion from 250nm to 0.8-1.2nm). When this program finishes the running, it will present the data like Figure 3.3. Those are reflectance and transmittance of the given order of diffraction. The disadvantage of this program is inconvenient to find the diffraction angle. We can input any incident angle in the calculation but it is not automatically reported the diffraction angle with those reflectance and transmittance in the result page. However, it can be calculated separately in this program at the Angles-Calc tap (we found out that the program calculates the angle of diffraction according to the Eq. (2.34)).

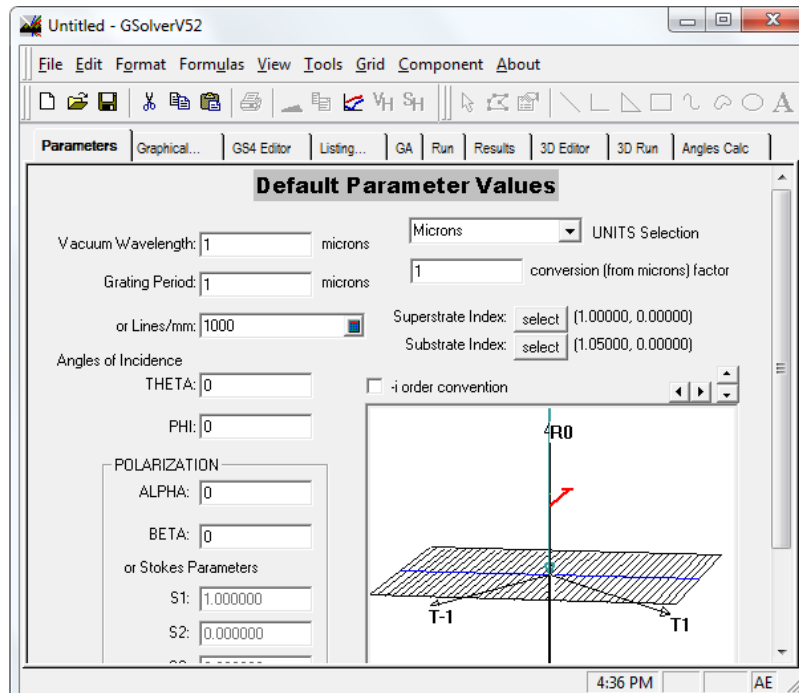


Figure 3.2 The window of G Solver program.

	OR	-1R	-2R	SumR	2T	1T	0T	-1T	-2T	SumT	Total	lambda
0.3800	0.040723190	0.000432115	0.000183310	0.041954042	0.000128665	0.001018003	0.565273425	0.001018003	0.000128665	0.567566763	0.609520805	0.380000
0.3850	0.072853175	0.000249008	0.000197685	0.073746564	0.000102219	0.001038165	0.552763541	0.001038165	0.000102219	0.555044311	0.628790875	0.385000
0.3900	0.106801958	0.000134943	0.000200723	0.107473292	6.13614268e-05	0.001047237	0.53681509	0.001047237	6.13614268e-05	0.539032288	0.646505580	0.390000
0.3950	0.136279626	0.000110968	0.000166691	0.136834947	2.88500162e-05	0.001048402	0.520664042	0.001048402	2.88500162e-05	0.522818546	0.659653492	0.395000
0.4000	0.155763755	0.000180660	0	0.156125077	0	0.001040366	0.504164215	0.001040366	0	0.506244948	0.662370025	0.400000
0.4050	0.157921697	0.000336466	0	0.158594631	-0	0.000994753	0.498464117	0.000994753	-0	0.500453624	0.659048254	0.405000
0.4100	0.153773323	0.000571657	0	0.154916639	-0	0.000951583	0.507231543	0.000951583	-0	0.509134711	0.664051349	0.410000
0.4150	0.141569544	0.000844001	0	0.143257547	-0	0.000929420	0.51803806	0.000929420	-0	0.519896902	0.663154448	0.415000
0.4200	0.120633804	0.001132142	0	0.12289809	-0	0.000918705	0.531664262	0.000918705	-0	0.533501673	0.656399763	0.420000
0.4250	0.094227137	0.001392623	0	0.097012384	-0	0.000908222	0.545387819	0.000908222	-0	0.547204265	0.644216648	0.425000
0.4300	0.067622188	0.001568451	0	0.070759090	-0	0.000888324	0.560067042	0.000888324	-0	0.561843691	0.632602781	0.430000
0.4350	0.042039114	0.001672315	0	0.045383745	-0	0.000890940	0.576886771	0.000890940	-0	0.578686853	0.624052398	0.435000
0.4400	0.021749340	0.001697358	0	0.025144058	-0	0.000888576	0.59001938	0.000888576	-0	0.591796532	0.616940590	0.440000
0.4450	0.010044375	0.001654798	0	0.013353972	-0	0.000868785	0.597481545	0.000868785	-0	0.599219117	0.612573089	0.445000
0.4500	0.008072273	0.001550237	0	0.011172748	-0	0.000839400	0.598659072	0.000839400	-0	0.600337873	0.6111510621	0.450000
0.4550	0.014955608	0.001403818	0	0.017763246	-0	0.000800699	0.594027754	0.000800699	-0	0.595629152	0.613392397	0.455000
0.4600	0.028380904	0.001237011	0	0.030854928	-0	0.000755105	0.584783224	0.000755105	-0	0.586293435	0.617148363	0.460000
0.4650	0.045334136	0.001071040	0	0.047476218	-0	0.000709165	0.572894736	0.000709165	-0	0.574313067	0.621789284	0.465000

Figure 3.3 The G Solver resulting window.

Even though G Solver use a numerical method such as Algebraic Eigenvalue to find reflectance and transmittance, but it also agree with thin film theory if it used to solve thin film problem. A single layer thin film is used to find this coherent. The configuration is as show in Figure 2.8 when $n_i = 1.33$, $n_f = 1.6$, $n_t = 2.0$, $d = 375nm$ and the incident angle is zero. The reflectance spectra from

GSolver and Eq. (2.22) for the single layer thin with incident wavelength from 380 to 750nm are the same thing as shown in

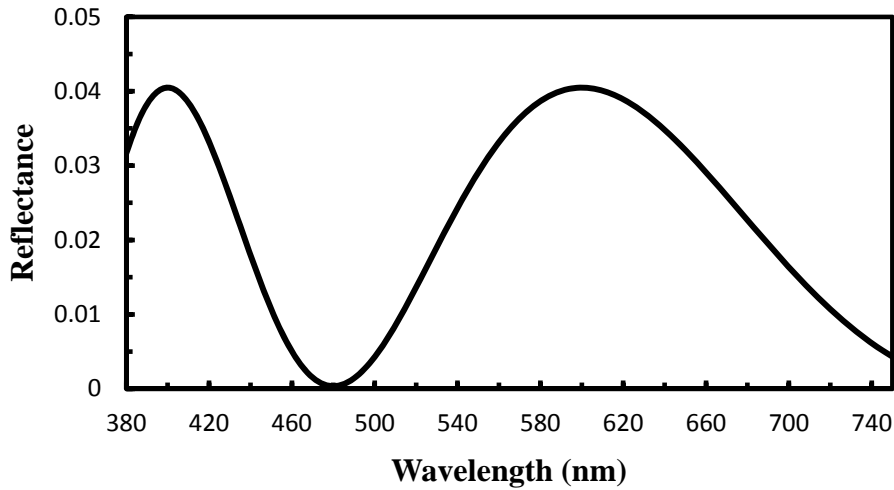


Figure 3.4 The single thin film reflectance spectrum from single, evaluated from Eq. (2.22)

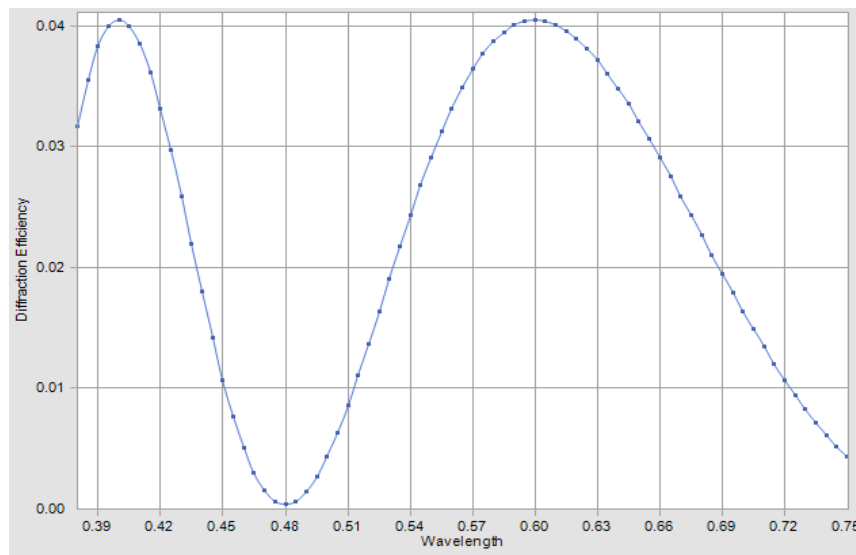


Figure 3.5 The single thin film reflectance spectrum from single, evaluated by G Solver. Diffraction efficiency is reflectance, and wavelength is in micron unit.

3.3 Refractive Index of PEDOT

GSolver the optical properties in n and k , but it does not contain PEDOT optical profile like Al_2O_3 and ITO. However, that data can be collected from the J. Hwang's paper [24]. It was reported with a graph with the conductivity (σ) and the absorption coefficient (α) instead of n and k , so it need to change the σ and α to n and k by applying Eq. (2.6) and (2.12). The values of σ and α are collected from the graph by using GetDat Graph Digitizer program to find the position data which illustrated in Figure 3.6. The original paper report the dispersion in wave number unit or cm^{-1} , it need to change to μm for GSolver calculation. After changing the unit and using the equation, it reveals the n and k profile of PEDOT like shown in Figure 3.7.

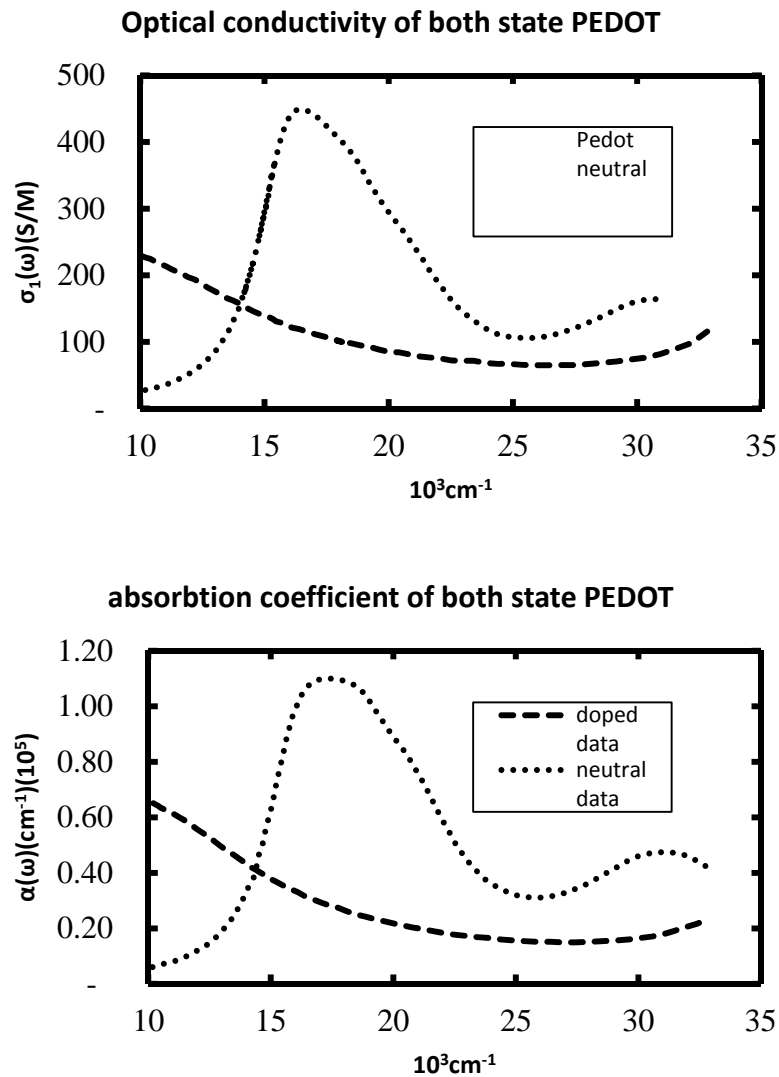


Figure 3.6 Optical conductivity (σ_1) and absorption coefficient (α) [24].

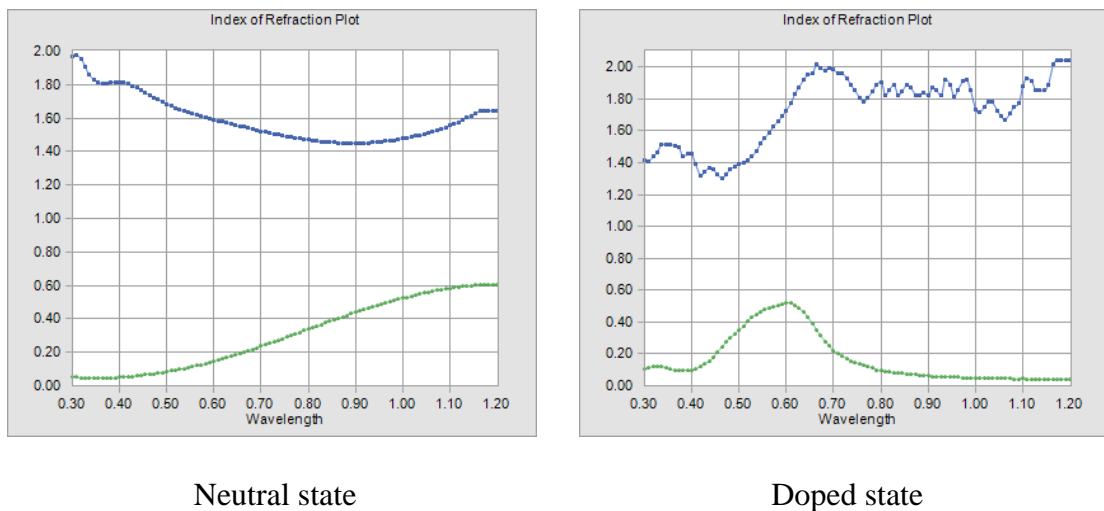


Figure 3.7 The PEDOT optical properties n (above line) and k (under line) that loaded to G Solver. This wavelength unit is micron.

3.4 Scope of Incident Light

The grating is a tool to diffract light. It usually appears the rainbow tap on the grating if the light imping on just one direction. However, it will be another if the light falls on to grating from many directions with the same intensity. This situation may occur to the grating when it is exposed by the light from the sky which are covered by the white cloud, or the reflected light from the white wall. Those are like the diffracted color on DVD grating that shown in Figure 3.8. The left in that figure is the diffraction from the one incident angle which show rainbow tab while the right is the diffraction from many reflected lights from the behind wall, impinging on the DVD in many directions. The later has not the rain bow tab, but it seems to an abstract paint color. The cause of this may come from the fact that many wavelength of light can be diffracted to the same angle; the color of that direction is mixed.

For the DVD, the diffracted light is the reflected light from grating, while our cause is transmitted light from our grating. So the observer of this study is in opposite side to the incident light as shown the configuration in Figure 3.9



Figure 3.8 Diffraction on DVD plate, from one incident angle (right) and from many (left).

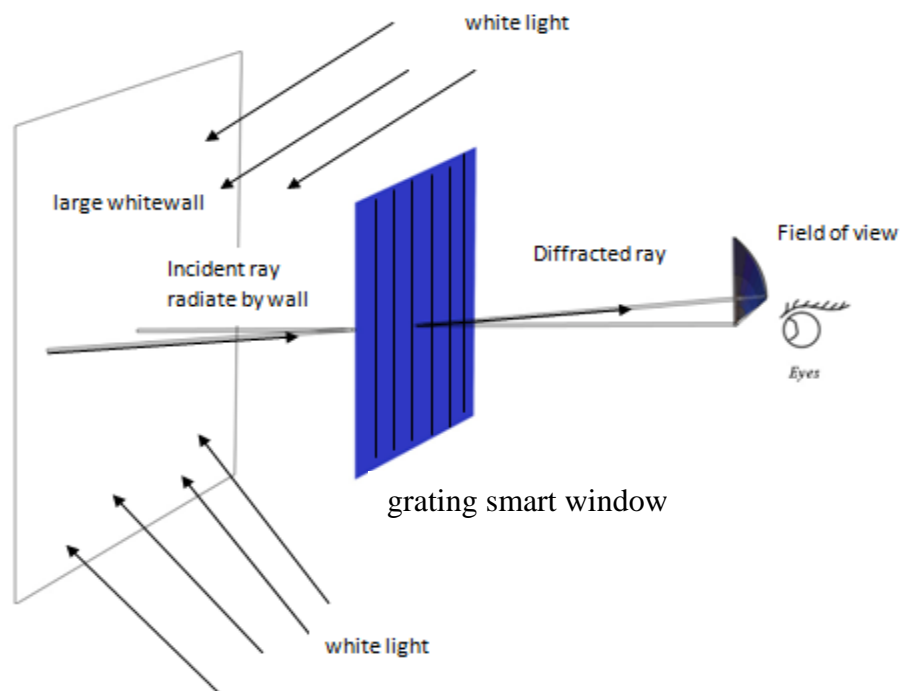


Figure 3.9 The configuration of this study, All incident angles from the wall impinging on grating structure and diffracted to the observer.

3.5 Angles

Angles are used to define the direction of the incident ray and transmitted ray. To define the angle in 3 dimension, it need 2 degree of freedom, that is θ and ϕ . If the grating place on xy plane, θ is the angle to tell how the ray is away from the z axis, ϕ is the angle between the projected ray to the xy plane and the x axis as shown in Figure 3.10.

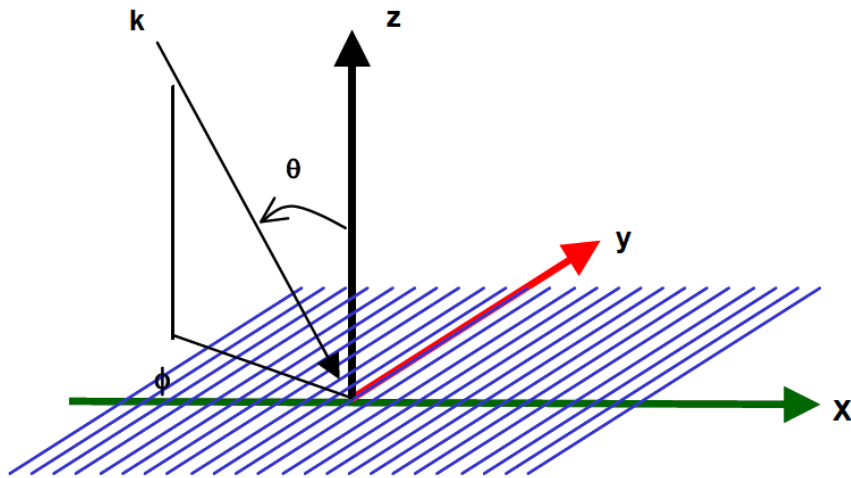


Figure 3.10 Angles definition.

In the simulation, we need the spectrum to draw the color along all transmitted angle, but GSolver cannot solve that directly. It cannot calculate the spectrum from given transmitted angle, but it calculates from the incident angle. Consequently, it need to find the incident angle from given transmitted angle and this can be done by using grating equations in Eq. (2.34). For our configuration (periodic along x axis), that equations is

$$\frac{2\pi n_t}{\lambda_0} \sin(\theta_t) \cos(\phi_t) = \frac{2\pi n_i}{\lambda_0} \sin(\theta_i) \cos(\phi_i) + \frac{2\pi m}{d_x} \quad (3.1)$$

$$\frac{2\pi n_t}{\lambda_0} \sin(\theta_t) \sin(\phi_t) = \frac{2\pi n_i}{\lambda_0} \sin(\theta_i) \sin(\phi_i)$$

Where index T and I refer to transmission and incident medium. With Eq. (3.1), the incident angle (θ_i, ϕ_i) can be found from diffraction angle (θ_t, ϕ_t) and wavelength λ_0 . After arrangement to find (θ_i, ϕ_i) , the new equations are

$$\phi_i = \tan^{-1}\left(\frac{d_x n_t \sin \theta_i \sin \phi_i}{d_x n_t \sin \theta_i \cos \theta_i + m\lambda}\right)$$

$$\theta_i = \sin^{-1}\left(\frac{d_x n_t \sin \theta_i \cos \phi_i + m\lambda}{d_x n_t \cos \phi_i}\right)$$
(3.2)

Fortunately, GSolver allow formula script like in Microsolf Excel, this will make the calculation more convenient. Finally, let denote that (,) refer to the pairs of angle, the first value is θ , later is ϕ .

3.6 Field of view

The field of view is color field that relate to the transmitted angle, and it represent the image that perceived by an observer’s eyes. In the eyes, there is the lens that can make the parallel light convert to the same point [25] as shown in Figure 3.11. We exploit this to the transmitted light from our grating structure. Many monochromatic lights that transmitted to the same angle would be converted to the same point. This is the basis idea of the field of view, each point on field of view relate to the transmitted angle and it should be draw as a circle. However, the radius of the circle is a problem, how radius of the field of view should it be to make it resemble as the real object if its picture is place before the eyes? From the fact that each point on field of view relate to the angle, we think that the field of view should be place at the position that make the points from the picture correspond to the angle that they calculated from as shown in Figure 3.12, then that field of view picture will resemble

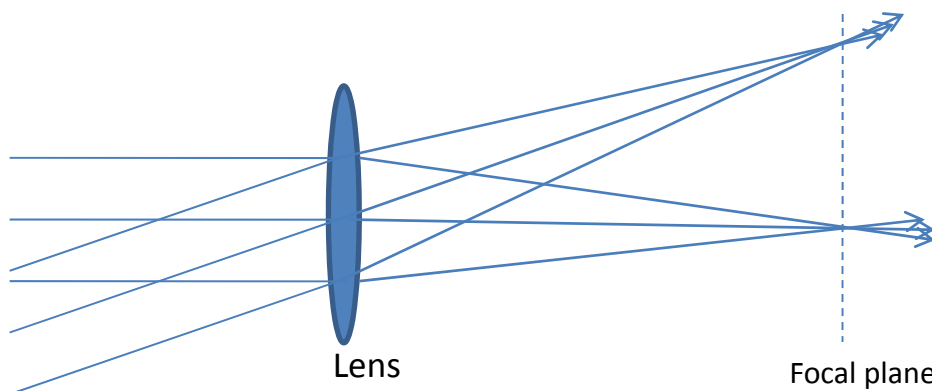


Figure 3.11 The parallel ray from grating, converting to the same point after the lens.

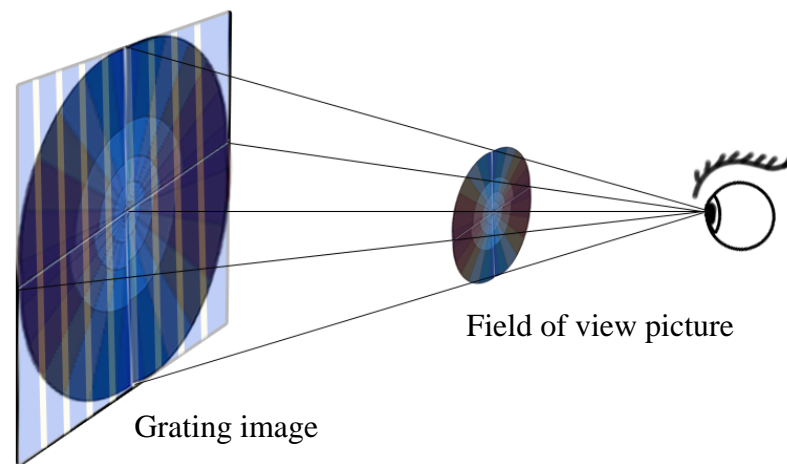


Figure 3.12 Resemble the color on grating via the field of view picture by moving it to the right position.

the image from the grating. Therefore the size of field of view can be any as long as we can move the picture to the right position. If it is larger radius, then the eyes just move away longer from that picture. We denote the radius of field of view by D and the angles coming from the transmitted angle (θ_t, ϕ_t) . From those two, the field of view can be written in the radial form as

$$r = D \tan \theta_t \hat{r} + \phi_t \hat{\phi} \quad (3.3)$$

like described in Figure 3.13. We can plot this in Ghost Script program which provide the radial drawing command. The pattern of diffraction from grating is symmetry, and for 1 or 2 dimensional grating, they have 2 symmetry axes. Consequently, using just 1st quadrant for drawing is enough to span the whole image. The 1st quadrant is divided to many section, each section correspond to the different transmitted angle as shown in Figure 3.14. The color of each section calculate from the angle of the center position of each section which be labeled in that figure.

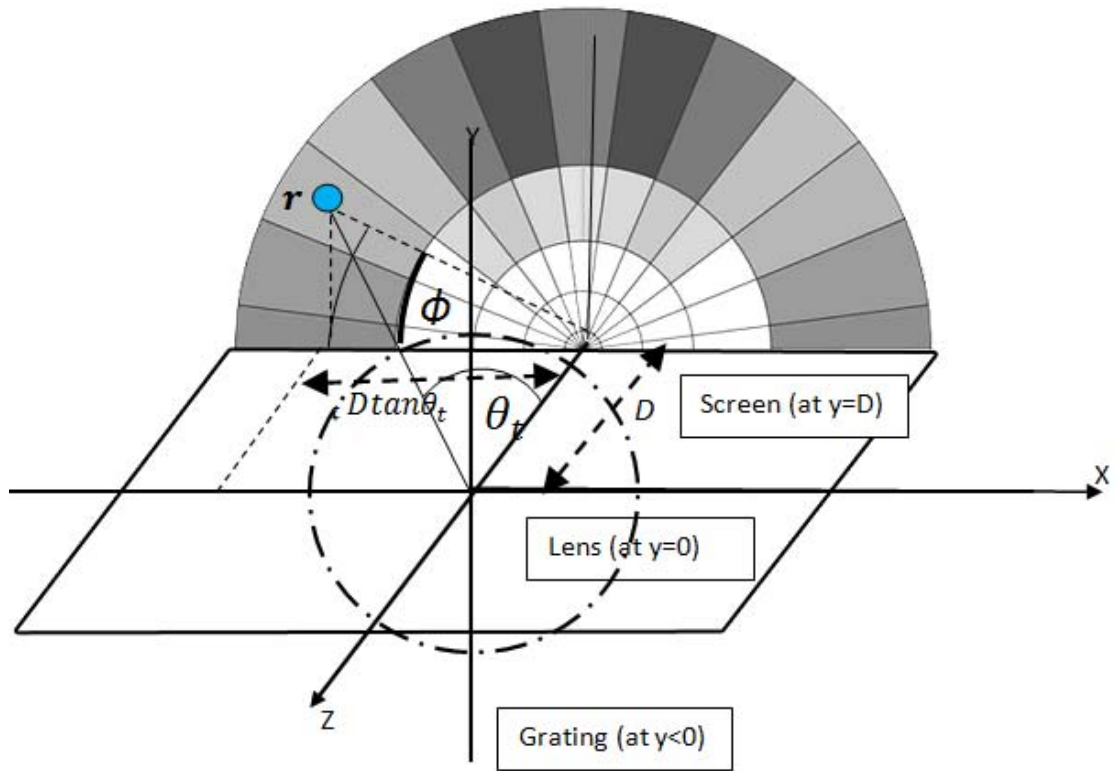


Figure 3.13 Radial coordinate of field of view.

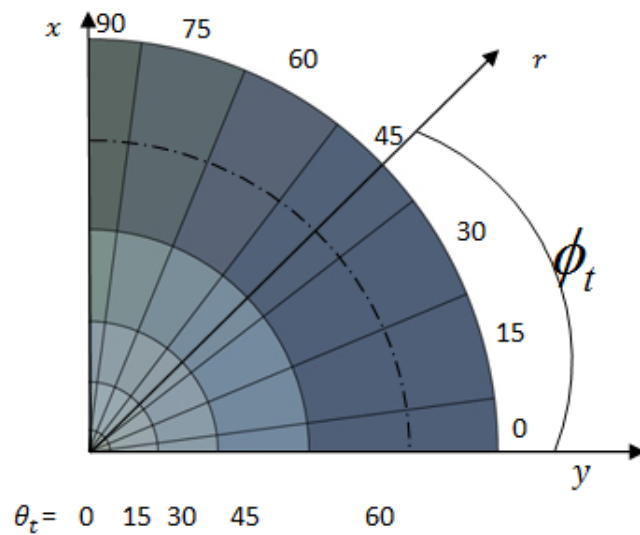


Figure 3.14 Relation between the section on field of view and the diffraction angle.

CHAPTER IV

RESULTS

The color of grating smart window, derive from the transmitted spectrum from 2 layers, grating (PEDOT and Al₂O₃) layer and ITO layer, between superstrate $n=1.3$ and substrate $n=1.5$. The incident spectrum to our grating structure is the sunlight spectrum, called D65, and fall on to grating in all direction. Those colors are represented in field of view which used to resemble the real image from the grating.

4.1 Spectra

Before calculate the color, it need to find the spectrum which can be calculated through GSolver. The transmitted angles of our calculation are $0 \leq \theta_t \leq 60$ and $0 \leq \theta_d \leq 90$, both of them step every 15 degree. The spectrum of any transmitted angles are come from zero-order ($m=0$) and first-order ($m=1,-1$) of diffraction. There are the other diffraction orders, but its intensity cannot compare to those two and can be neglected. In this study, the spectrum from zero-order is called main spectrum and noise spectrum for the first-order. The separated spectrum is more helpful in analysis than the merge spectrum. Some angles have only main spectrum without noise spectrum because all the incident angle cannot diffracted to that transmitted angle at that wavelength. For example, the diffraction angle (45,30), have only main spectrum because the θ_i from the grating equation, Eq. (3.2), is undefined when $m = 1$ or -1 . Only the following diffraction angles can have the noise spectrum, i.e., (0°,0°), (15°,0°), (15°,15°), (15°,30°), (15°,45°), (30°,45°), (15°,60°), (30°,60°), (15°,75°), (30°,75°), (15°,90°), (30°,90°) and (45°,90°). The spectrum from all transmitted angles are calculated, but only (0°,0°), (30°,0°), (30°,45°) and (30°,90°) are shown in this book for comparison. Those positions of those selected angle in the field of view are represented by the circles as shown in Figure 4.1.

The main and noise transmittance spectrum of structures A,B and C from $(0^\circ,0^\circ)$, $(30^\circ,0^\circ)$, $(30^\circ,45^\circ)$ and $(30^\circ,90^\circ)$ diffraction angles are shown in Figure 4.2- Figure 4.4 respectively. Each graph also compares the noise spectrum and the main spectrum of neutral state and doped state. For the main spectrum, the doped state is much higher than the neutral state, except it tail. The neutral state is higher around the wavelength 400nm and 700nm. It seem that there is similarity in between the angle when consider from the main spectrum. The spectrum from $(0,0)$ and $(30,90)$ are similar to each another. It is also for $(30,0)$ and $(30,45)$ as well. The main spectrum is always higher than zero unlike the noise spectrum. The noise spectrum also have similarity in the angle $(0,0)$ and $(30,90)$ but not for the others angle. Considering the whole spectrum results of each structure, spectra from A and B are similar in shape to each another for both neutral and doped states. However, some angle is different in the noise spectrum, the A seem to be higher than the B in the angle $(30,45)$. The comparison of each spectrum from those two structure at all observed angle farther (which don't show in this book) also reveal that when the angle $\theta_d = 60$, their spectra are look very different in the noise spectrum. It quite corresponds to the color result in the field of view (compare between Figure 4.8 and Figure 4.9). Even though A and B spectra curve is look very similar, but they are slightly different. The A spectrum is a little lower than the B spectrum in the neutral state and it may lead color to be darker. However, it can anticipate that those which have similar spectrum may represent similar color. In contrast, structure C spectrum is obviously different from those two. It also have similarity in between angles $(0,0)$ - $(30,90)$ and $(30,0)$ - $(30,45)$, also similar but the spectrum from the pair $(0,0)$ - $(30,90)$ of structure C is similar to and $(30,0)$ - $(30,45)$ of structures A and B. Hence structure C would have similar color to structures A and B but the color alignment may be different from the others structure.

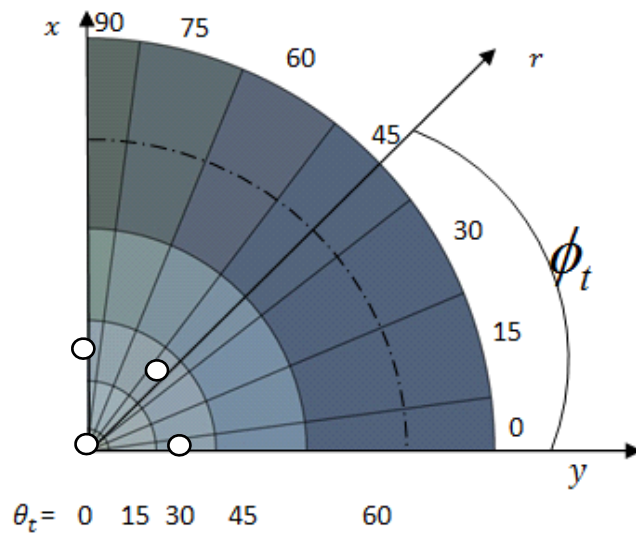


Figure 4.1 Selected point for spectrum representation to the field of view.

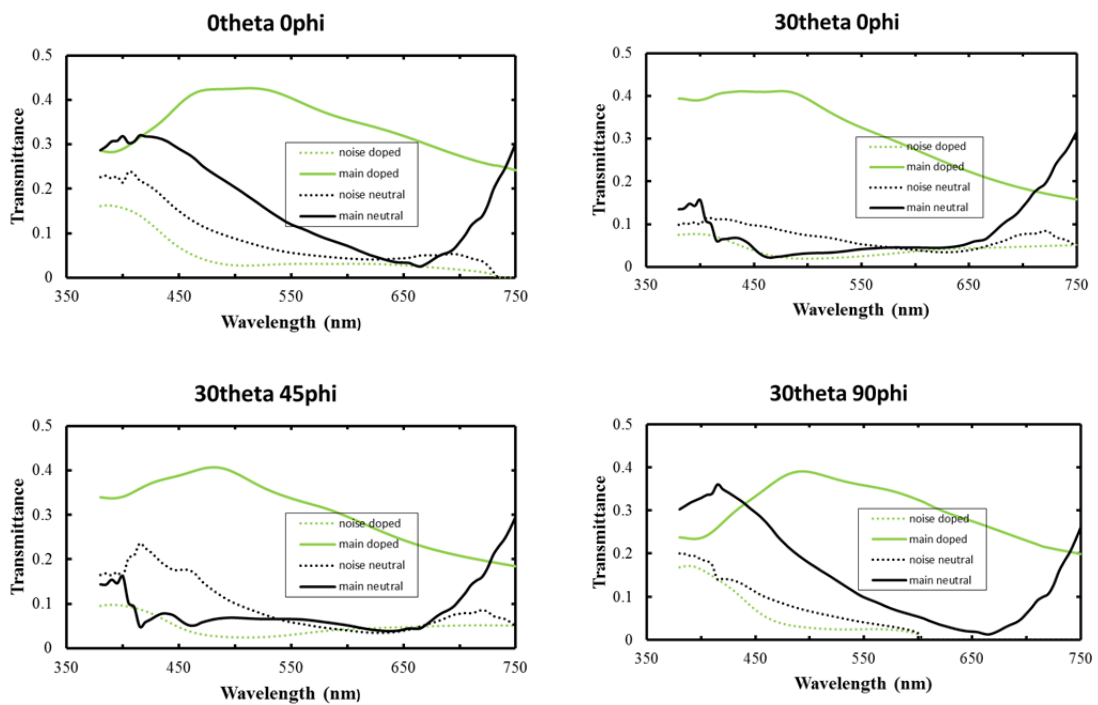


Figure 4.2 Main and noise spectra from structure A for neutral (N) and doped (D) PEDOT at (0,0), (15,0), (15,45), and (15,90) diffraction angles

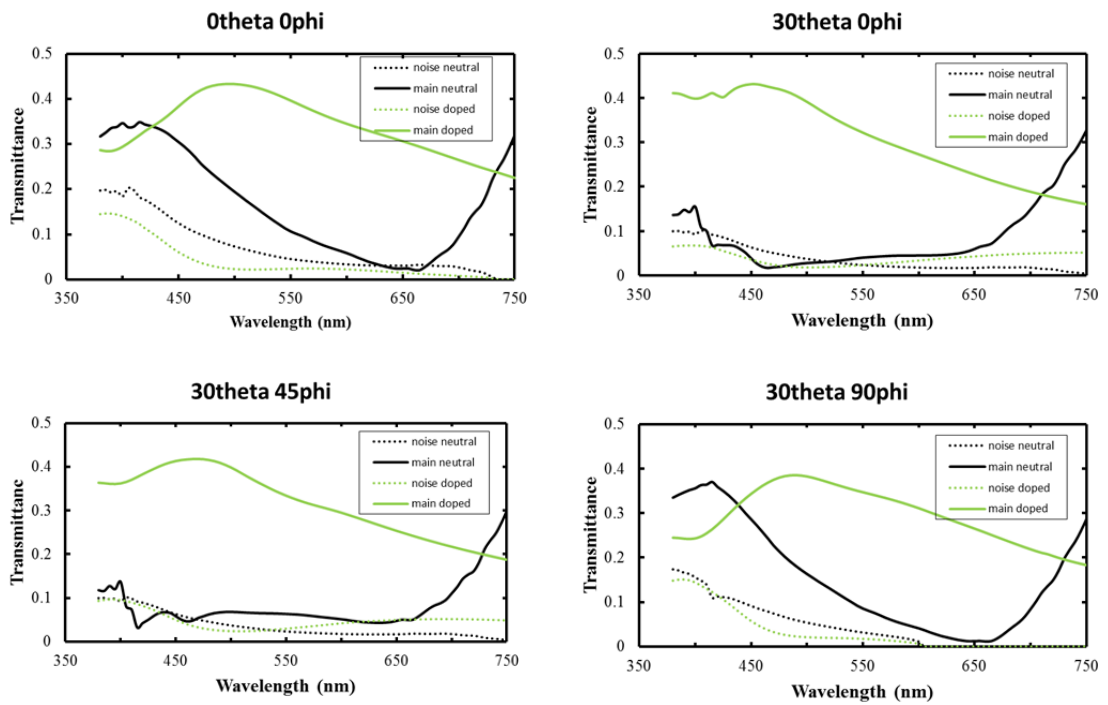


Figure 4.3 Main and noise spectra from structure B for neutral (N) and doped (D) PEDOT at (0,0),(15,0),(15,45) and (15,90) diffraction angles.

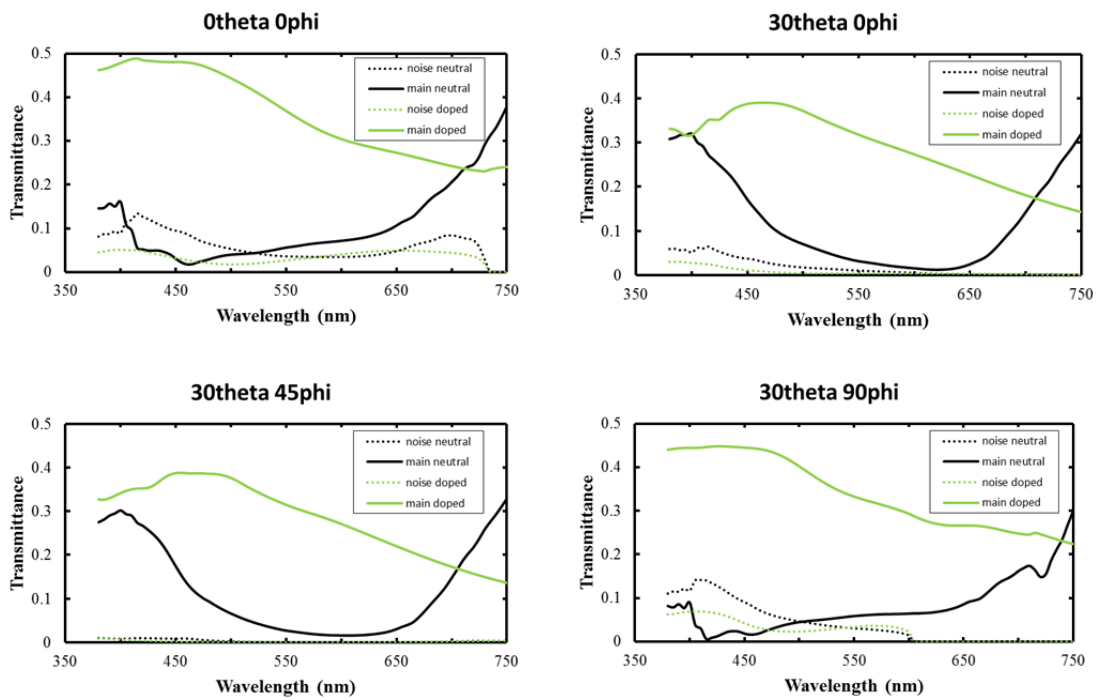


Figure 4.4 Main and noise spectra from structure C for neutral (N) and doped (D) PEDOT at (0,0),(15,0),(15,45) and (15,90) diffraction angles.

From the grating equation, it state that the wavelength that approximately longer than the grating period is not diffracted. It may lead to confuse that why grating with 550nm period can have noise spectrum, which come from the diffraction, of the longer wavelength. It is because that noise spectra is calculated from the various incident angles which can be diffracted to the transmitted angle like shown in Figure 4.5. It may think that the light see the period of grating be longer when it impinging at the oblique angle. Therefore, the longer wavelength can have the transmittance because it can be diffracted.

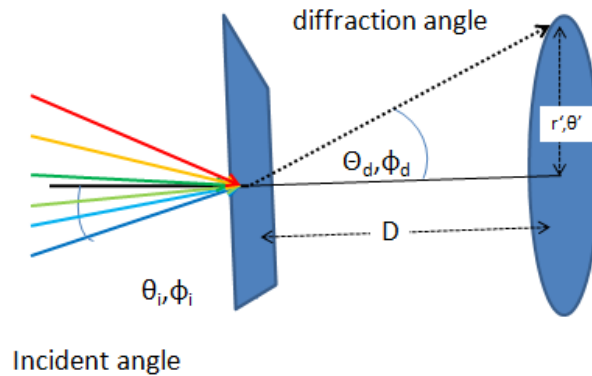


Figure 4.5 Depict many incident angles that can be diffracted to the same diffraction (transmission) angle.

It is hard to comprehend the main and noise spectrum curve from our structure. However, one can notice that the main spectra curve correspond to the extinction coefficient (k) of PEDOT in both state, which shown in Figure 2.7. It is because the extinction coefficient tell about how much the light is absorbed, higher k value correspond low transmittance. For example, the neutral main spectra of structures A and B in the angles (0,0) and (30,90) have the crest around 600 like the k of neutral PEDOT. The spectra from those angles are also suspicious, why they are similar even though those angles are different. The reason may come from the fact that the period of those angles are not different to the incident light, Figure 4.6. However, there is the different of the neutral main spectrum from (0,0) and (30,90), the intensity from (30,90) seem to be lower. It is because the transmitted light from (30,90)

propagate more distance in PEDOT and lead to more absorbed. In the other hand, the neutral main spectrum from angle (30,0) and (30,45) are more complicate, their intensity decrease farther than (0,0) and (30,90). This may be described by using the intensity equation for grating (Eq. (2.31)). Besides the configuration parameter, the intensity is also depend on the number of the slit or N , it proportional to N^2 . Consequently, it is possible to think that the N of angle (30,0) and (30,45), somehow, are lower than (0,0) and (30,90) angle. The intensity equation also state that the spectrum of zero-order(main) always higher than the first-order(noise), and it is according to the graph except the neutral spectrum of (30,0) and (30,45) angles. Around 400-480nm of those angles, the noise spectrum shows little higher than the main spectrum. It probably because the incident angles of the noise spectrum at that wavelength are close to zero, which give N larger than the main spectrum. Consequently, the intensity of noise spectrum becomes higher.

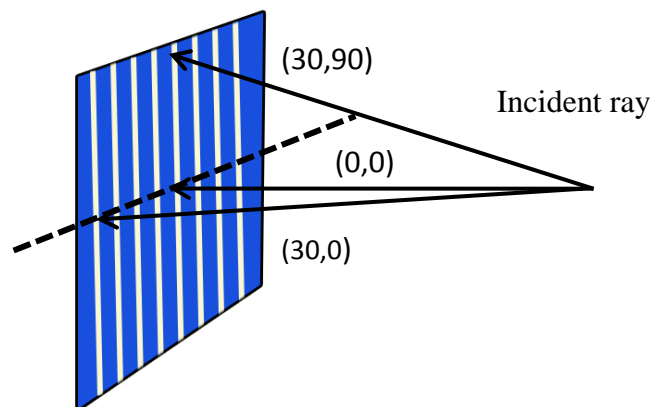


Figure 4.6 The incident ray (0,0) and (30,90) realize the same period length of grating

Even though Al_2O_3 and PEDOT in doped state are transparent, but the grating from that materials still has the effect from the diffraction because they are not completely similar in optical properties. Consequently, the noise spectrum still exists but quite low because the optical properties of those materials are close together. The tail of all noise spectra always decrease unlike the main spectrum. It is so because the longer wavelength of noise spectrum propagates the high incident angle. It mean that it propagate in PEDOT longer and be more absorbed. Some wavelength of noise spectrum may drop to zero because it is not satisfy the grating equation (Eq.(2.27)).

Structure C is very extra ordinary because it switches the result and seems that the normal grating equation cannot interpret the result from structure C. We cannot understand why the spectrum from (0,0) of structure C is similar to (30) of structure A. We try to use the rays that propagate through our grating structure as shown Figure 4.7 to get some idea. From the figure, the ray that imping on structure A at the angle (30,0) (ray2) and the ray from structure C at the angle (0,0)(ray3) propagate through the materials with the same order. The ray 3 propagates from Al₂O₃-ITO-PEDOT that similar to the ray 2, while the ray 1 and 4 is from Al₂O₃-ITO-Al₂O₃. This is just the guess idea but it seems to have a reason.

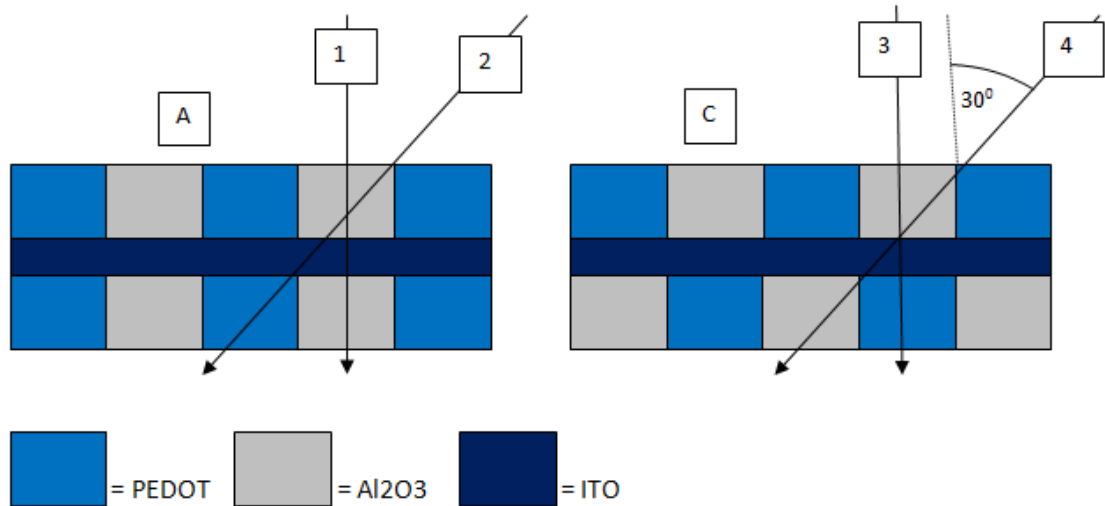


Figure 4.7 Depict the material that the ray propagates through. Al₂O₃-ITO-Al₂O₃ for the ray 1 and 4 and Al₂O₃-ITO-PEDOT for the ray 2 and 3.

4.2 Field of View Color

All spectra of each direction are transformed to color through the colorimetry method and the field of view will be drawn in first-quarter as written in chapter 3. It will reveal what color on grating to the observer. The field of view from 3 structures is reported and include with normal structure. The normal structure that has just PEDOT in grating layer is used in order to comparison between the grating smart window and traditional smart window.

From all result, structures A,B,C and structures with their both state seem that a longer radius color at the longest radius have deep or darker color compare to a lower radius color. The longer radius proportion to the larger angle, the light will propagate more distance and be more absorbed and become darker. All the color on structure A, B and C are rather colorful when they are in neutral state. In the other hand, the doped state seems to have a homogeneous color, but there is a dim dissimilar color appears around the vertical axis. This nonhomogeneous color does not appear in the normal structure. Among of grating structures, structure C seem to have rather homogeneous than the others.

In neutral state, the color of from structure A as shown in Figure 4.8 is rather homogeneous blue when $\theta_d < 30^\circ$, while the farther angle gives various color appearance, i.e., purple, brown and green. A Color of the angles that close to vertical axis which θ_d is around 75° - 90° is similar to blue color. The color appearance of structure B is very similar to structure A. However they are different in the saturation at the high degree $\theta_d = 60$. Structure B seems to have low saturation than structure A. The cause of this is the higher of noise spectrum which can be noticed from (60,0) of structure B, as shown in Figure, lead the brightness higher and the color become lose the saturation. In contrast, the color appearance of structure C is different, the color around the center is rather colorful than those two structure as shown in Figure 4.10. The blue tone is along the (60,60)-(30,0) angle instead vertical axis and the overall color is similar to structure B which lack of saturation. Hence, we can conclude that double layer grating structure like B and C provide the less saturation color to the smart window. However, amount of all structure, neutral from the normal structure show the most saturate because it show the most dark color. The color of all fields of view is evaluated for present by the normal LCD with sRGB gamut.

The printer, which have different gamut, may present the color different from the LCD, but this different is just a little.

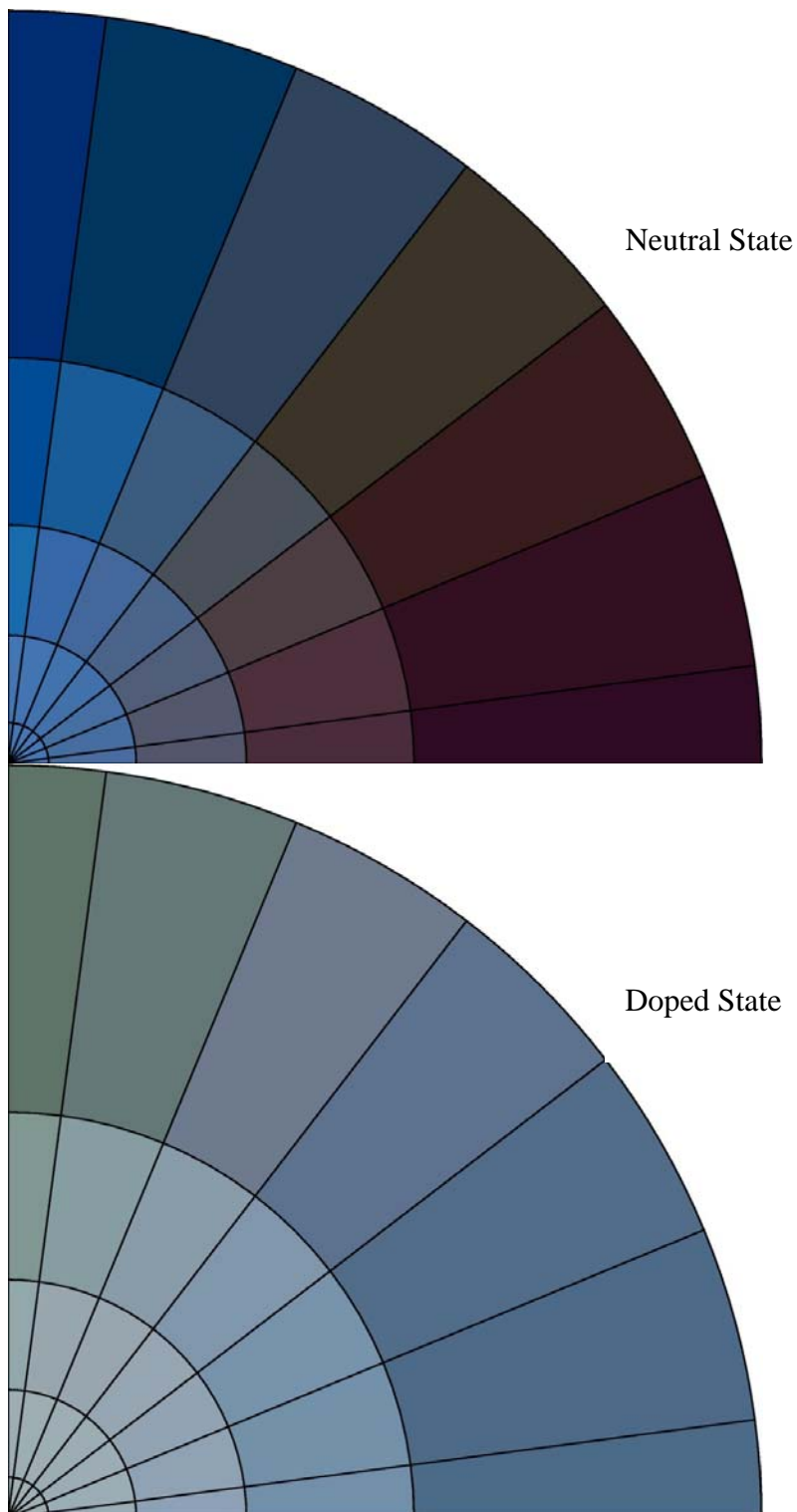


Figure 4.8 Field of view of structure A when period = 550 nm and grating thickness = 700 nm. The superstrate and substrate is 1.33 and 1.5 respectively.

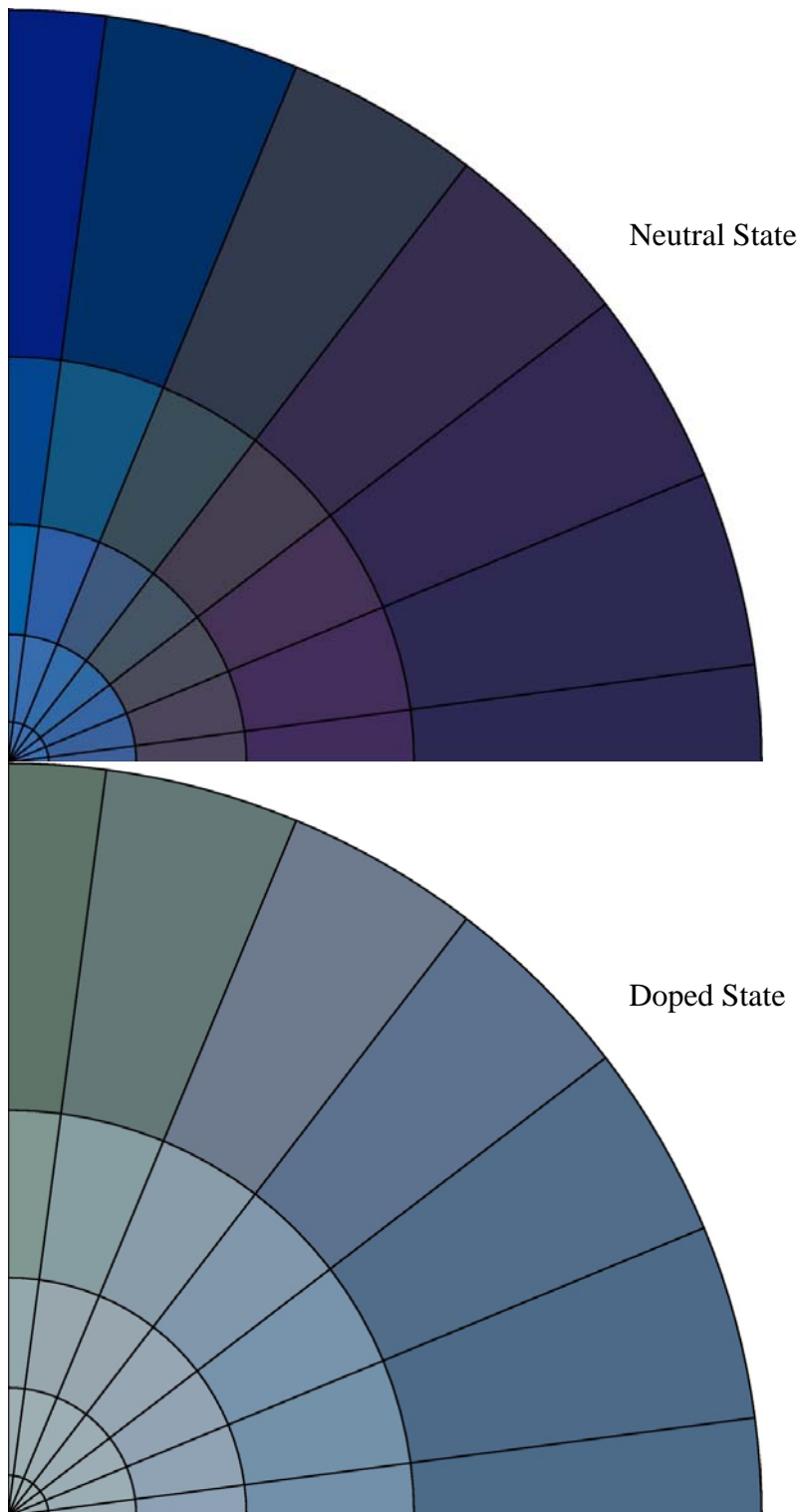


Figure 4.9 Field of view of structure B when period = 550 nm and grating thickness of top and bottom are 350 nm. The superstrate and substrate are 1.33.

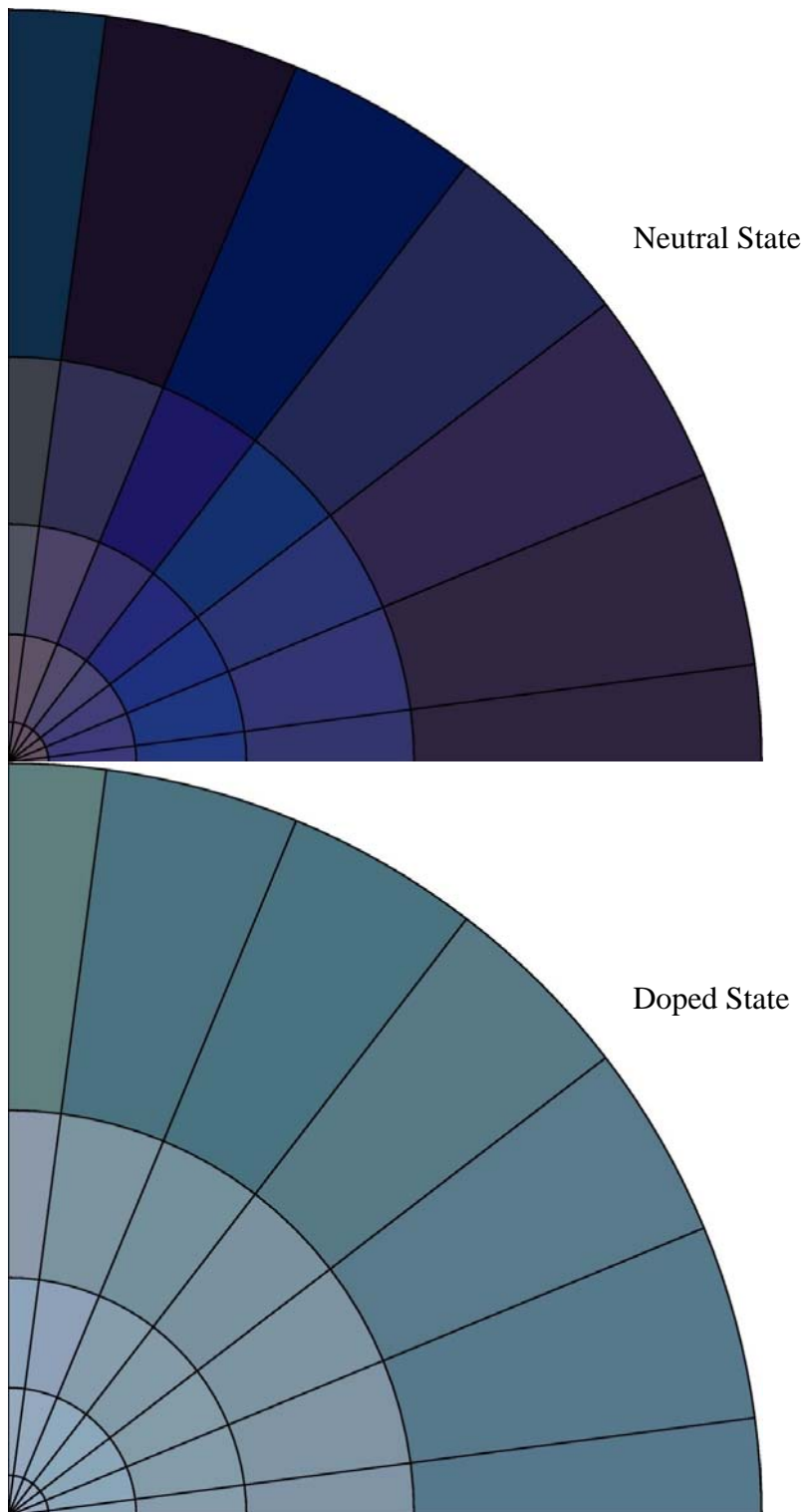


Figure 4.10 Field of view of structure B when period = 550 nm and grating thickness of top and bottom are 350 nm. The superstrate and substrate are 1.33.

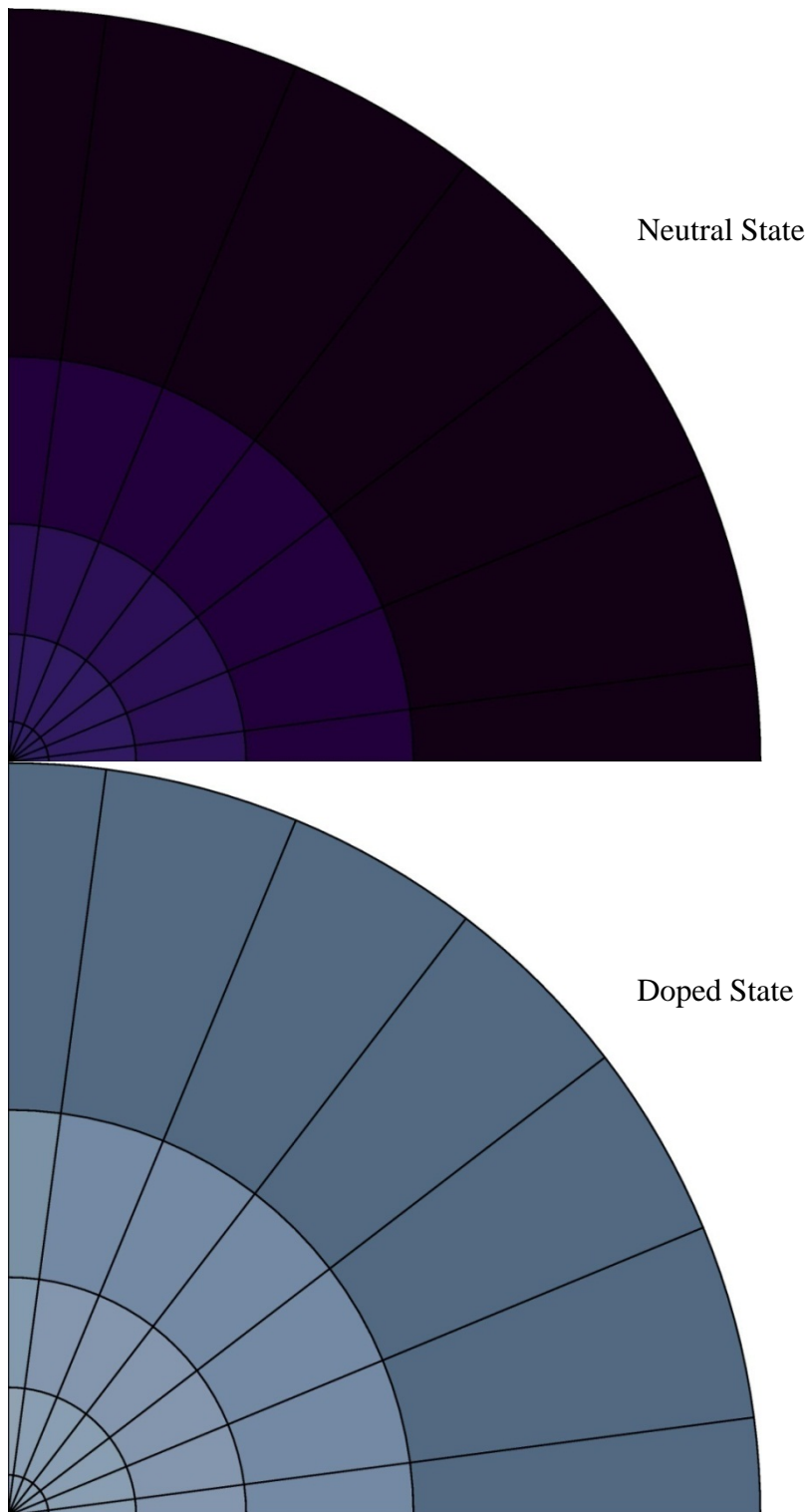


Figure 4.11 Field of view of normal structure(a structure without Al_2O_3). No period length and the thickness of PEDOT layer = 350 nm. The refractive indices of superstrate and substrate are 1.33 and 1.5, respectively.

4.3 Luminance and contrast

One factor that is important for the smart window is the brightness which can be interpreted in luminance. A luminance value can be collected from the Y value in XYZ color index. The ratio of the luminance between the neutral state and doped can be acknowledged as light controlling ability. We call it as contrast which can be defined as.

$$\text{Contrast} = 100\left(1 - \frac{Y_{\text{neutral}}}{Y_{\text{doped}}}\right)$$

The contrast is set between 100 and 0. The highest value mean the light cannot propagate out from the window in neutral state which is the best in light controlling ability. On the other hand, the lowest value mean there is no different in transmitted light between the neutral state and the doped state.

The luminance and contrast of field of view from Figure 4.8 - Figure 4.11 are represented in Figure 4.12 - Figure 4.14. The horizontal axis is the angle θ_d and each line on that figure refer to the angle ϕ_d . All luminance from that figures, both neutral and doped, main and noise spectrum, show that they decrease when the angle θ_d increase. It is correspond to darker color on the field of view with the same reason. Among of the grating structure, structure A shows the highest in the average luminance of each angle ϕ_d , structure B and structure C are lower respectively. To explain the highest luminance from structure A, it probably is the effect from the number of layer that the light propagate through. From the superstrate to the substrate, the light propagates through structure A by 2 layers, but 3 layers when it is structure B. More transition layer mean more reflected lights, and if they are in phase, it will make the intensity higher. That corresponds to the lower transmittance, thus the luminance of structure B is lower. The luminance is different in angle ϕ_d when θ_d is equal. It is similar to the different spectrum in the angles (30,0) and (30,45). The reason may affect from the N number and the ray path of the noise spectrum. Dissimilar to the neutral, the doped luminance show a little diversion. It is probably because a little different between the doped PEDOT and Al_2O_3 optical properties. When the both luminance from each state are transformed to the contrast, it quite opposite to the luminance, the highest average contrast seem to be structure C, structure B and A are lower respectively. It means that structure C gives the light controlling ability better

than structures A and B. It means that C is the most comfortable to grating smart window in the light controlling. However the normal structure is better in that ability than all grating structures.

In our luminance and contrast result, their values when $\theta_d = 0$ are the same. It is so because we use the circular polarization which makes the light independent to ϕ_i when $\theta_d = 0$. When we use the linear polarization, we observe that when $\theta_d = 0$ the transmittance is depend on ϕ_i . This cannot be described from the classical grating theory, but it does so as it reported (Figure A.1 [37]) . It may be similar to the different in s and p polarization of reflected as describe in chapter 2. In contrast, the light from the sunlight does not depend on that angle. The sun is the unpolarized light which have random the polarize direction while the circular polarization is not. Those two are not equivalent but this study is just approximation. Thus, we use the circular polarization in order to avoid that problem when $\theta_d = 0$.

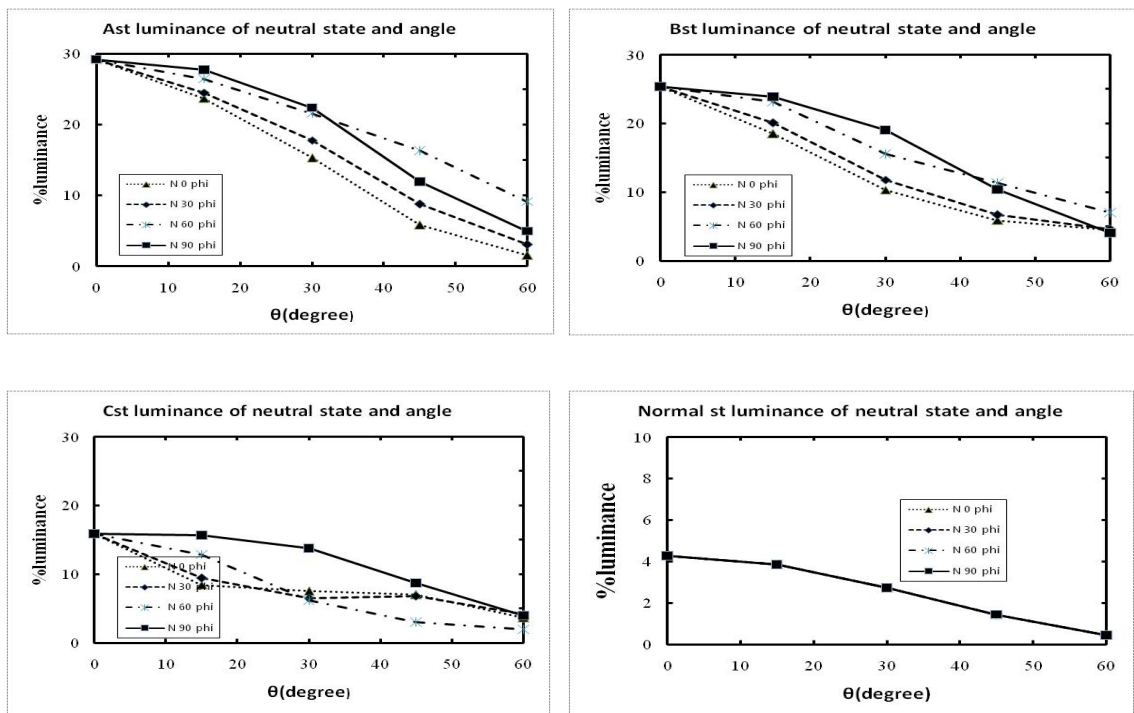


Figure 4.12 Represent the luminance for neutral PEDOT in all observed angle for structures A,B,C and normal.

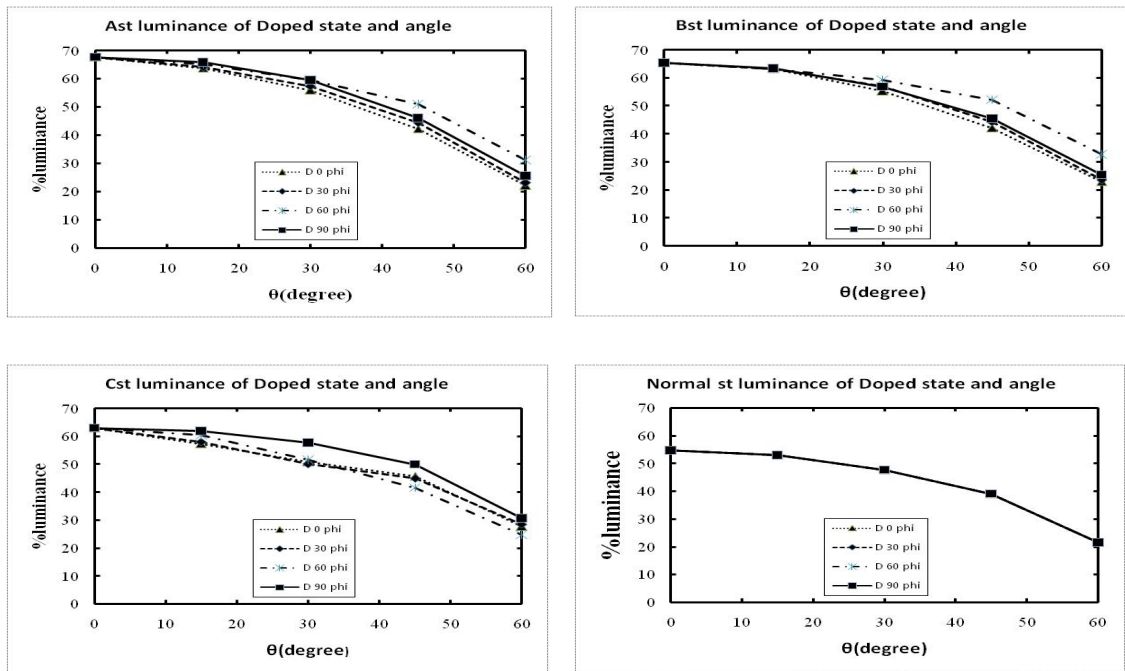


Figure 4.13 Represent luminance for doped PEDOT in all observed angle for structures A,B,C and normal.

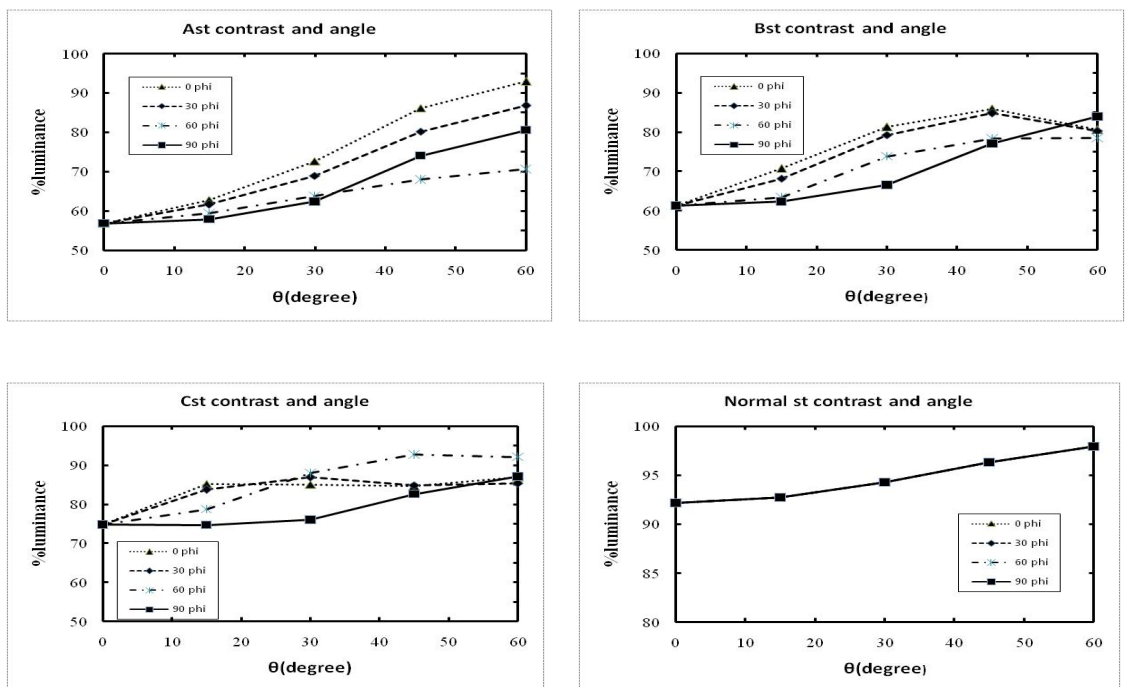


Figure 4.14 Represent contrast of PEDOT in all observed angle for structures A,B,C and normal.

4.4 Discussion

We also attempt to describe the transmitted spectrum from our grating. We concentrate in our structure A when the incident angle is zero, it correspond to angle (0,0). To analyze with classical theory, we assume that the grating layer of structure A is just homogeneous layer of PEDOT or Al₂O₃ like Figure 2.9. Therefore we can use thin film theory for double thin film. Therefore, we derive the transmittance from the Eq. (2.22) like the reflectance in Eq. (2.30). The problem is arise from the coefficient t that should be lower than 1. The coefficient t_3 is

$$t_3 = \frac{2n_{ITO}}{n_{ITO} + n_{Al_2O_3}}$$

The definition of t_3 is the amplitude of the incident electric field in ITO (E_i^{ITO}) divided by the transmitted electric field in Al₂O₃ ($E_t^{Al_2O_3}$). The electric field $E_t^{Al_2O_3}$ is always lower than E_i^{ITO} because the energy distribution from the reflectance. Hence t_3 is lower than 1. In our case, n_{ITO} is larger than $n_{Al_2O_3}$, it make t_3 greater than 1! It is so trouble because it contrasts to our case. Hence, we use the reflectance, which always lower than 1 in any case, to avoid this problem.

According from the relation $1=R+T+A$, the slope of transmittance should be inverse to the reflectance. It seems to be like that when compares the T from the simulation to the classical calculation of neutral PEDOT as shown in Figure 4.15. Especially, it rather agrees with that relation at the wavelength more than 500, but it disagree for the lower wavelength. We also find the spectrum when the period of grating structure is very small. That thing can be treated as the homogeneous material from PEDOT and Al₂O₃. To find the optical properties in the case like that, we apply the volume average to our materials to find the effective optical properties

$$n_{eff} = \frac{1}{2}(A + \sqrt{A^2 + B^2})$$

$$k_{eff} = \frac{1}{2}(-A + \sqrt{A^2 + B^2})$$

where

$$A = P(n_{PEDOT}^2 - k_{PEDOT}^2) + (1 - P)(n_{Al_2O_3}^2 - k_{Al_2O_3}^2),$$

$$B = 2n_{PEDOT}k_{PEDOT}P + 2n_{Al_2O_3}k_{Al_2O_3}(1 - P),$$

P is the porosity; it is 0.5 to our cause. The spectrum from the effective optical properties is similar to the case of just PEDOT. The inverse of the slope between R and T seem to start at 550 nm. Hence, we can describe the spectrum from the grating by use the effective properties when the wavelength is greater than 550nm. Notice that our grating period is also 550nm. It is probably because the light of higher wavelength feels the grating layer as a homogeneous layer. However, the effective theory cannot apply to the wavelength that lower than the period, it is disagree like shown in Figure 4.16

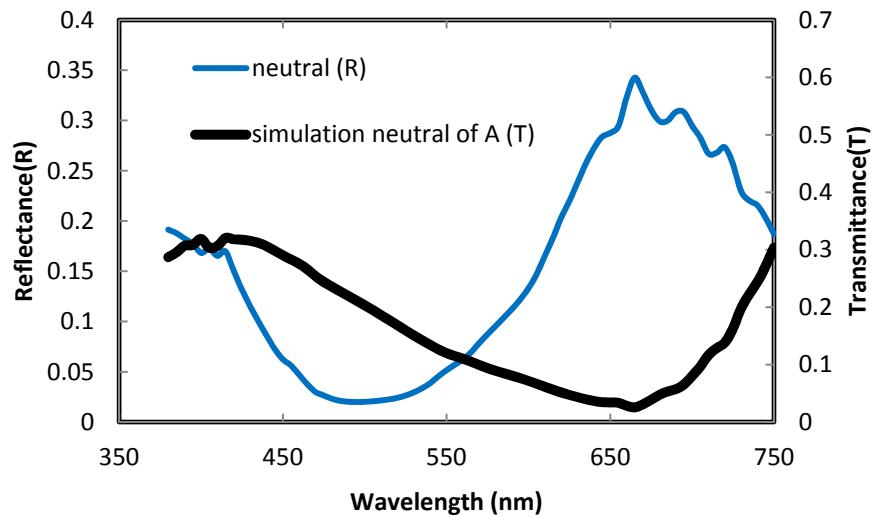


Figure 4.15 The transmittance from the simulation and the reflectance from thin film theory when the top layer is neutral PEDOT.

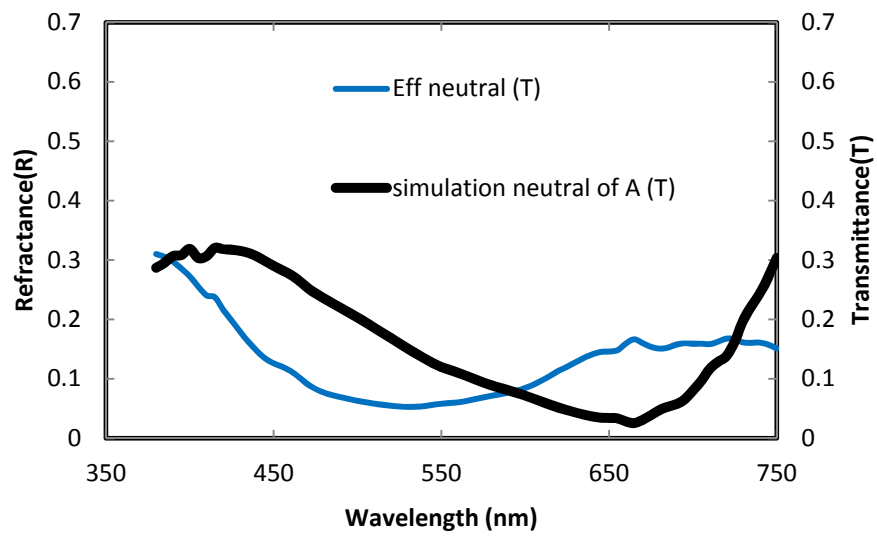


Figure 4.16 The transmittance from the simulation and the reflectance from thin film theory when the top layer is effective medium from neutral PEDOT and Al_2O_3

CHAPTER V

CONCLUSIONS

This thesis has started with the simple hypothesis that the smart window can be made from the grating structure, periodic from Al_2O_3 and the electrochromic material, PEDOT. We studied this in order to find the feasibility to make the new type of smart window. There are so many electrochromic materials, but PEDOT is selected because it shows the high light controlling ability and gives high switching time between its transparent state (neutral) and dim state (doped). We investigate by using the diffraction calculation from GSolver to simulate the transmitted spectrum from the grating smart window. It can be converted to the color index and luminance. D65 sunlight spectrum is used as the incident light in order to simulate the transmission diffraction under the sunlight. In order to find the color that the human can respond in the eye, we use the idea of parallel transmitted light will convert to one point after the eye lens. The diffracted lights from grating structure that transmitted to the same angle are the parallel light in our case. The spectrum of any angle is made from the monochromatic wavelength that diffracted to that angle. We can calculate the all angle by the grating equation that covers the angle in three dimensions. That spectrum from that will be transformed to XYZ color index by the CIE XYZ colorimetry in order to represent the color.

Three grating structures, A; B and C, which quite similar to each other are investigated. The results from those are also compared to a normal smart window structure which has only PEDOT in the structure without Al_2O_3 in electrochromic layer. The transmitted spectra are reported in form of the main spectrum (first-order of diffraction) and the noise spectrum (zero-order of diffraction). The tail of the main spectrum is according to the extinction coefficient. In contrast, the tail of the noise spectrum always drops because those wavelengths come from the high incident angle; they propagate longer distance in the structure. It corresponds to be more absorbed and make the transmittance drop. The spectra from structures A and B are analogous; it

corresponds to color similarity. For the color appearance on field of view when PEDOT is in neutral state, structure A in neutral state look alike to structure B that the blue color is near the center (angle (0,0)) and vertical axis while the others angle give various color such as purple, brown and green. There are also various colors in neutral state of structure C, but it is different in some way from the A and B. One also can notice that the color from structures B and C in neutral state are less saturate than structure A, so the double grating layer like structures B and C may not be a good choice for smart window when concern its color. However, the colors of doped state of all structures seem to be homogeneous like the normal structure. Accordingly, the color on the doped state may show just one color like the normal smart window while the neutral state gives various colors. Therefore, it may prove that the grating smart window can be the application of window like the normal. The luminance that comes from the Y value in XYZ color index is used in order to describe the brightness. For luminance in neutral state and doped state, each structure show that $A > B > C > \text{normal}$. In light controlling ability or the contrast, it is evaluated from luminance ratio between the neutral state and the doped state. In that result, structure C is the highest in amount of the grating structures, B and A are next respectively. Thus, we may have two choices for the grating smart window that is saturated color but lack the contrast, which is structure A, or the opposite that is structure C. However, for the contrast, the grating structure cannot compare this ability to the normal.

By application the thin film theory to the grating smart window, it seems that it can apply when the wavelength is larger than the grating period, 550nm. We investigate this when the incident angle is zero. We think that the value may increase for the oblique incident angle because the period becomes larger to the light.

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APPENDIX

GRATING WAVEGUIDE STRUCTURE

There is some kind of grating structure that can make the reflectance or transmittance reach near to the extreme values, 0 or 1. It is the structure that called a grating waveguide structure. It can be made from the grating layer and the transparent thin layer. Those two need to be stick together. An anomalous peak from the grating waveguide is a sharp peak as shown in Figure A.1. It reaches an extreme value when the resonance condition is fulfilled. A reflection filter [38] and a security marks [39] are its application. Beside, Cunningham *et al.* have already accomplished to use it as a biosensor [40]. When the bio molecule reacts with particular material that coat at superstrate or substrate, it affects to those refractive indexes and causes the anomalous peak shifting. The refractive index will change and cause shifting of anomalous peak. In biosensor field, it proper to find the reflectance instead the transmittance because, sometime, the substrate is the absorbed material. It makes the peak drop in its high and the sensing ability may decrease.

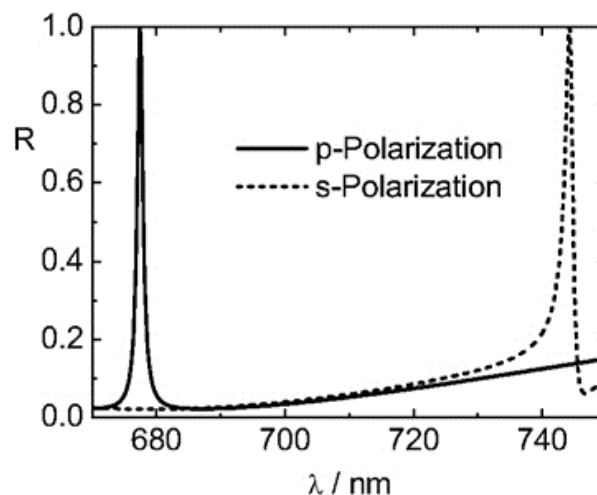


Figure A.1. Anomalous peak from transparent grating waveguide structure. Both p and s polarizations have its own condition for that peak [37].

The 1D grating waveguide structure is illustrated by (Figure A.2). The light imping in superstrate (I) which has refractive index n_I . The light is diffracted by

the grating layer (II), thickness d_g and same refractive index as region III. The below the grating layer (III) is a transparent homogeneous layer, called the waveguide layer with thickness d_f , and its refractive index n_f is greater than the others layers. The light transmits to the substrate (IV), refractive index n_{III} . Some time, the layer II can be waveguide and layer III is the grating. Such structure gives the high reflectance spectrum, so it needs to find the anomalous drop instead

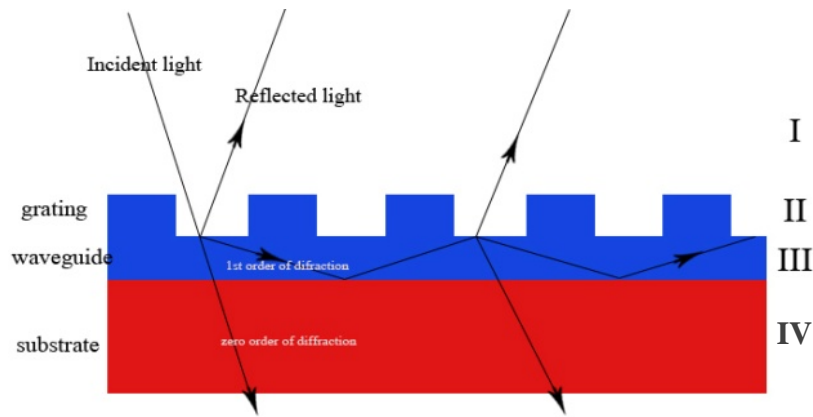


Figure A.2. Grating waveguide structure.

The mechanism of the resonant condition is very simple. When the light propagated to the interface of air and grating, both of transmission and reflection can be diffracted from grating according to equations

$$R: \sin\theta_r = n_I \sin\theta_i + \frac{M\lambda}{n_I \Lambda},$$

$$R: \sin\theta_r = n_I \sin\theta_i + \frac{M\lambda}{n_I \Lambda},$$

$$T: \sin\theta_t = \frac{n_I}{n_f} \sin\theta_i + \frac{M\lambda}{n_f \Lambda}, \quad (\text{A.1})$$

$$M = 0, \pm 1, \pm 2, \dots$$

Where Λ mean the grating period and M is the order of diffraction. In the waveguide layer (III), the transmitted light from the first-order and others order except zero-order will be totally reflected back to the grating layer (II). This is so because the higher refractive index of that layer. That light will be diffracted again and some is reflected back to the waveguide layer as shown in Figure A.2, and this process repeatedly occurs. These reflected light lose some intensity by changing the medium. However,

the other reflected light can compensate that lose if the optical path of those reflected light are in phase. This is the anomalous reflectance peak. The anomalous drop occur when those optical path are out of phase. There are 2 optical phase gain, first is the optical path in the waveguide that is $\frac{4\pi}{\lambda}n_f d_f \cos\theta_t$. Notice that the angle is the diffraction angle instead of the incident. The additional phase comes from additional from the reflection from the region I and IV ($2\phi_{fI}$ and $2\phi_{fIV}$) to the region II. Therefore the resonance condition is

$$\frac{4\pi}{\lambda}n_f d_f \cos\theta_t + 2\phi_{fI} + 2\phi_{fIV} = 2j\pi ; j = 0,1,2, \dots \quad (\text{A.2})$$

When the light is s polarization

$$\phi_{fI} = \tan^{-1}\left(\frac{(\Lambda n_I \sin\theta_i \pm \lambda_0)^2 - n_I^2 \Lambda^2}{n_f^2 \Lambda^2 - (\Lambda n_I \sin\theta_i \pm \lambda_0)^2}\right), \phi_{23} = \tan^{-1}\left(\frac{(\Lambda n_I \sin\theta_i \pm \lambda_0)^2 - n_{IV}^2 \Lambda^2}{n_f^2 \Lambda^2 - (\Lambda n_I \sin\theta_i \pm \lambda_0)^2}\right) \quad (\text{A.3})$$

The condition of the peak is very strictly, so the peak is really sharp like a stick.

We also use GSolver to simulate the spectrum from the transparent grating waveguide structure. It is agree with the resonance condition. However, this is not comfortable to our grating structure that emphasize in luminance and color. Even though the grating waveguide structure generate high peak but it is in very short wavelength which may not disturb the whole color. Furthermore, the ITO layer and the grating layer are an absorbed material. Hence the diffracted light may not compensate like previous and it will make the peak drop dramatically.

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