

# Optoelectronics-JR

Based on lecture of Jason Reilly

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# 1 Introduction to Color

## 1.1 Light

Color is defined as the subjective appearance of light that was detected by our eyes. The theory of light was developed, throughout the history. Young provide evidence that light can be thought of as waves, a lot of phenomenon such as reflection can be explained using wave theory. The euqation for light as a wave was shown below. Where  $\mathbf{k}$  is the wavevector, it can be calculated suing equation 1.3. N.B. 0 in the equation means in vacuum. Other terminologies are frequency  $f_0(\nu_0)$ ,  $\omega_0$  is angular frequency.  $c$  is the speed of light.

$$E_x = E_{0x} \cos(\mathbf{k}z - \omega t) \quad (1.1)$$

$$E_y = E_{0y} \cos(\mathbf{k}z - \omega t) \quad (1.2)$$

$$k = \frac{2\pi}{\lambda} \quad (1.3)$$

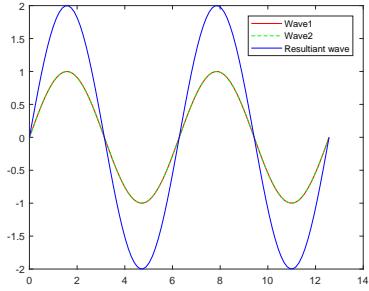


Figure 1: Constructive interference

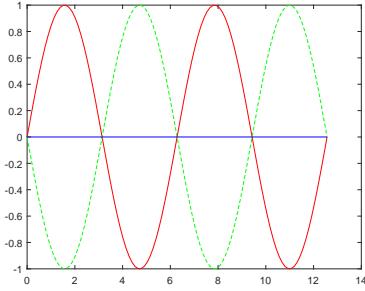


Figure 2: Destructive interference

However, wave theory cannot explain the 'Photoelectric effect', so Einstein proposed a new theory, saying that light consists of *Photons*. It says that each photons has fixed energy, this energy can be obtained by shining light on metals, and measure the Kinetic energy of the photoelectron. The energy of the photon can be calculated using euqation 1.4. And The photon energy was found to be proportional to the frequency of the light frequency  $\nu$ . As illustrated in equation 1.5

$$E_{el} = E_{ph} - \Phi \quad (1.4)$$

$$E_{ph} = h\nu \quad (1.5)$$

Apart from that, classical theory cannot explain the *ultraviolet catastrophe* phenomenon, according to Rayleigh-Jeans law, for a black body, the energy density  $\rho_E$  of photon with wavelength  $\lambda$  is equal to equation 1.6, if you want more information, refere to MSE-105.

$$\rho_E = \frac{8\pi kT}{\lambda^4} \quad (1.6)$$

This means the energy density will tend to infinity as wavelength approaches zero. There are infinite amount of ultraviolet light surrounding us, this is definitely not true. Maxwell solve this problem by letting the energy of photon to be *quantized*, photon can be thought like a harmonic oscillator, the low  $\lambda$  oscillator, which has very high energy, it must possess enough quanta to get excited, thus the probability for them to excite decrease exponentially as  $\lambda \rightarrow 0$ . Overall, the  $\rho_E$  is given by equation 1.7, this is the

$$\rho(\lambda) = \frac{8\pi hc}{\lambda^5 \exp(e^{hc/\lambda kT} - 1)} \quad (1.7)$$

**N.B.** In the black body, the peak shifts LHS as temperature increase. Before moving onto the next topic, we shall look at some terminology.

**Definition 1.1.** Monochromatic light consists of photons with a very narrow range of wavelengths.

**Definition 1.2.** Coherent wave means all waves in a beam are in phase.

**Definition 1.3.** Linearly Polarised means the electric field vector remains in one plane, i believe that it means  $E_{0x}$  and  $E_{0y}$  will not change as light progress, we shall recap this in the future.

**Definition 1.4.** Irrandiance  $I$  was defined as in equation 1.8

**Definition 1.5.** Energy Density  $E$  was defined as in euqation 1.9

$$I = KE_0^2 \quad (1.8)$$

$$E = \varepsilon E_0^2 \quad (1.9)$$

## 1.2 Vision

Light is perceived by eye-brain combination. The physiological response to light was as follows: light was perceived in the inner surface of the eye, wherre the retina was located. There is a compound in retina, called rhodopsin, which turn red-purple when light was received. The vasion was due to a set of complex reactions, which take place in two types of cells-rod and cones. Since human has three type of light receptor(for high light intensity), we are said to be trichromatic.

**Definition 1.6.** Rod cell is not sensitive to color and give rise to a monochromatic color, it saturates at high light intenisty, it is responsible for dark vision.

**Definition 1.7.** Cone cell is responsible for day vision, there are three variants of cones: L-cones, it has a absorbance peak at 560nm(in fact, it is most sensitive to yellow), responsible for red light. M cones, has absorbance peak at 530 nm, sensitive to and responsible for green light. S cones, absorbance peak at 420 nm, sensitive to blue light, peak at 420 nm. They are illustrated in figure 3. [2]

Note that human are most sensitive to the green light, this is the contribution due to both the red rod and the green rod, which lies closely together. While our eye is the least sensitive to blue light. You need a high intensity of blue light to activate the blue cone.

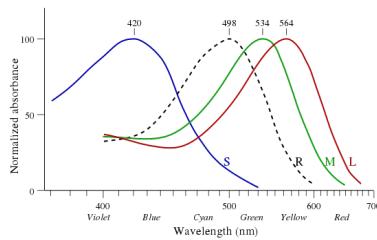


Figure 3: Cones and Rod, relative sensitivity, normalised

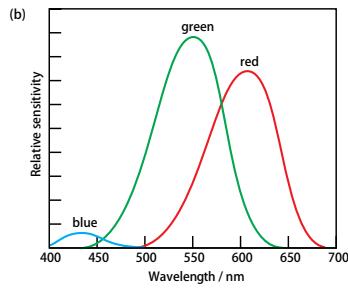


Figure 4: Sensitivity of rod

### 1.3 Three model of light

Our eye are very sensitive to light, by varying the combination of different photons slightly, the resultant color will be very different. Our eye can distinguish around 1 million different colors. So it is very difficult to express light quantitatively. Nevertheless, People found that all the colors can be expressed in terms of three parameters, these parameter forms a *Color space*. In this note we will explain three different models used to describe light quantitatively.

### 1.4 Hue, Saturation and Brightness(HSB model)

The first method is using a color whell.

**Definition 1.8.** Hue correspond to the wavelength or frequency of the light, correspond to the angle of figure 5. The angle starts at prime red ( $0^\circ$ ), to green ( $120^\circ$ ), then to blue ( $240^\circ$ ) and back to red.

**Definition 1.9.** Saturation is by how much the light was mixed with the 'white light'. It correspond to the radius of figure 5

**Definition 1.10.** Brightness describes the intensity of the light. It correspond to the number in the verticle axis of figure 5.

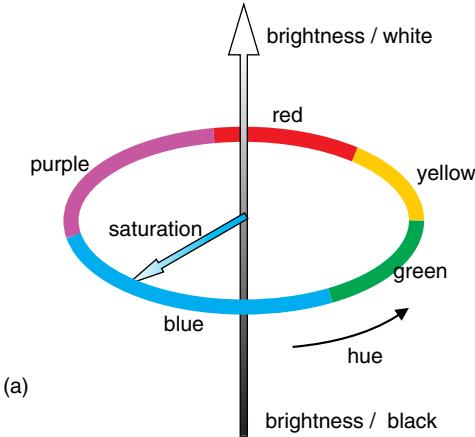


Figure 5: A color whell

#### 1.4.1 RGB model

First people proposed a color triangle model, as illustrated below

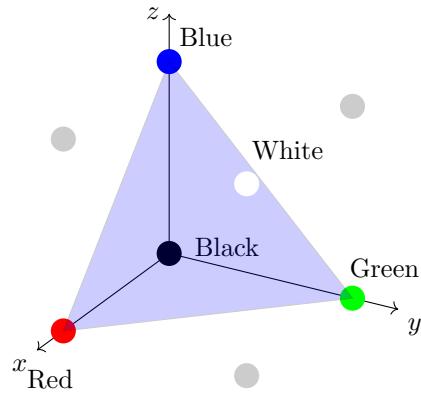


Figure 6: Color triangle

With this model, you make a cube, the  $(0,0,0)$  position correspond to black,  $(1,1,1)$  coordinate correspond to white, the  $(1,0,0)$ ,  $(1,0,1)$  and  $(0,0,1)$  coordinate correspond to the Red, green and blue respectively. Each point in the blue triangle (color triangle) actually represents all color that can be obtained by mixing the red, green and blue color (you can just use lever's rule to obtain the exact composition). But note that it only represent part of all lights, so a better model, the RGB model was explained below.

The RGB color model is an *additive color model*. As proposed by Com-

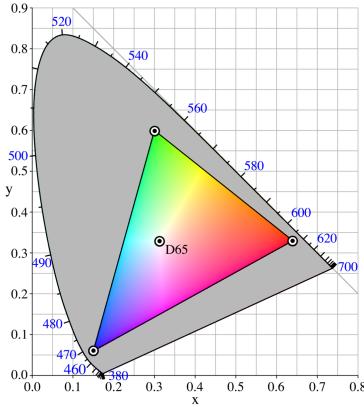


Figure 7: The outer edge of the hyperbola represents the *monochromatic* light, and the *Color triangle*.

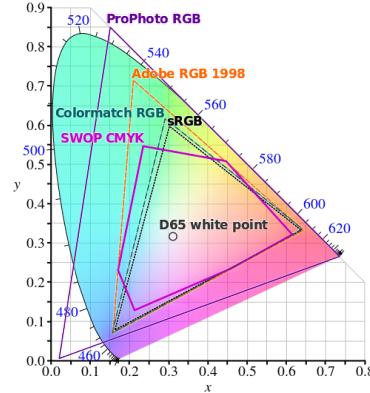


Figure 8: Second.

mission Internationale de l'Eclairage (CIE). It uses three basis color, which are reasonably monochromatic, and every color within the triangle can be produced by mixing differnet amount of these color. But it can produce every color within the color triangle. Shown in figure 7. Note that differnet devices uses differnet source to produce light, so they might produce slightly different light for given set of (R,G,B). And note that we still need to specify the 'Brightness' to fully specify a color. This model was used for cathode ray tube(CRT) displays. Note that if you raw a line of figure 8 through the white point(e.g. 480nm-580nm), you can use lever rule to know what fraction of light is needed to obtain any color within this line.

#### 1.4.2 CMYK Model

CMYK model is a *subtractive* color model, It was used in prints or reflective and transmittive device (big white screen at back, and light was taken away), it uses four inks: Cyan(*Negative red*), Yellow(*Negative blue*), Magenta(*Negative green*) and Key(*Black*). If you want a cyan color, you print the cyan, it absorb all the red light, you are left with blue and green, which appears cyan. Note for RGB, you can switch all off to get black, switch all on to get white, but you can't for CYM, so a 'key'(black) color is needed to absorb all light.

### 1.5 Pixel

**Definition 1.11.** A Pixel is the smallest addressable unit of a screen that can display different colours(can be made to be any color within the triangle). It consists of subpixel

**Definition 1.12.** Sub-Pixel In a colour display each pixel is made up of subpixels of differing color.

If you want to subtractive display and you need blue light, you need to take away 2/3 of light to produce blue for the horizontal subpixel. So vertically stacked reflective display is better, because light can come through directly. But if one subpixel was switched on, it cannot interfere with others, this is almost impossible to achieve in reality.

### 1.5.1 Electronic 'Paper'

To understand how Kindle work, consider figure 9a and 9b, it consists of liquids with two electrodes. In the liquid, there is some  $\text{TiO}_2$ (-ve) and Carbon (+ve), if you apply a negative potential, the top plate will become negatively charged, it attracts the carbon to the top, then it is similarly to pencil ink on top. But in fact paper is better, it is 64% reflective, kindle reached 58%. But to build a color kindle, you need three of these unit, each correspond to one of RGB, but once you have done that, 1/3 of the energy was wasted.

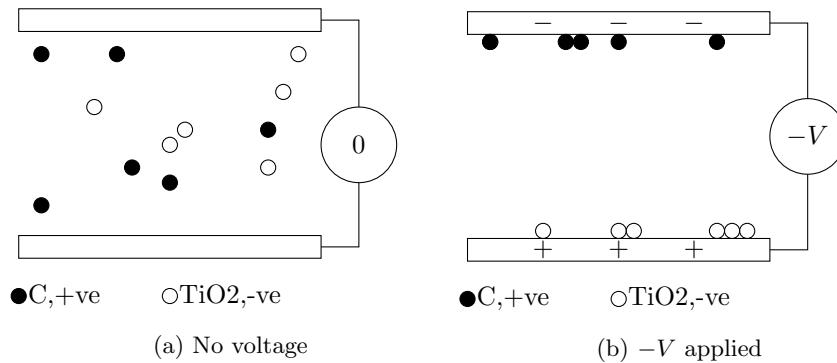


Figure 9

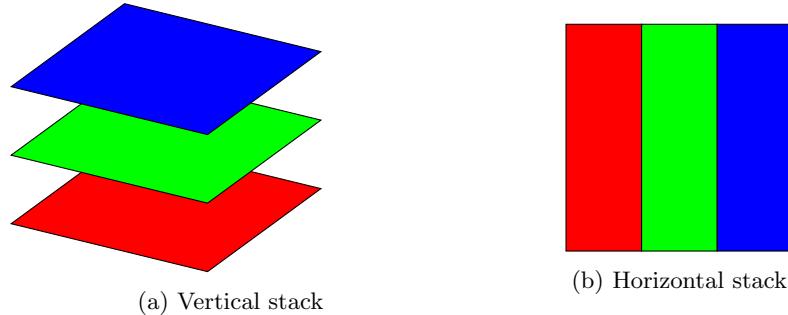


Figure 10

## 2 Color of different materials

### 2.1 Color of atoms

The content below need some familiarity with MSE-105 Quantum mechanics. We will first look at hydrogen atom, as illustrated in figure 11 (a). Which is the simplest atom in our world. Since it only has one electron, it has no shielding effect. The color is associated with moving electrons between different *energy* levels. Decrease in e.g. vibration will produce light in IR.

As light incident, it will get absorbed, the electron goes to excited state, and fall down, this process emits light. It turns out that if electron fall to the  $n=1$  state(Lyman series), it will produce UV light, if electron fall to  $n=3$  state (Paschen series), it will produce IR. It will produce light only if it falls to  $n=2$ , this is called Balmer series.

The sodium spectrum(figure 11 (b)) is slightly different, as it contains multiple electron. The electrons with lower angular momentum shield the high angular momentum electron. So there is an energy difference between 3s and 3p orbital. N.B. *photon carries an angular momentum of 1*, this implies as electron go down in 1 energy level, it has to change  $l$  by 1. Now the transition from 3s to 3p orbital produce orange light. If we look closely in the spectra, we can find a double line. This is due to the spin orbit coupling. The electron in the 1s orbital can orbit clockwise or anticlockwise(this result in two magnetic field with opposite direction), and the electron in the p can spin in two opposite direction, if the magnetic field align parallel to each other, the energy is differnt as if it align antiparallel. This result in a split in the spectra.

**N.B.** hydrogen and sodium atom's absorbtion and emission spectra are the same.

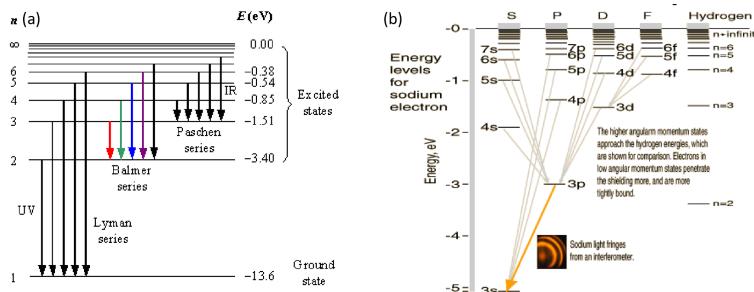


Figure 11: (a) schematic of orbits of H atom, (b) schematic of orbits of Na atom.

### 2.2 Color of molecule

Why are trees green? The answer is that trees has chlorophyll. There are two types of chlorophyll, chlorophyll a and b, as shown in figure 12. They differ by just one group. Chlorophyll a has a H<sub>3</sub>C group, whilst b has a aldehyde group.

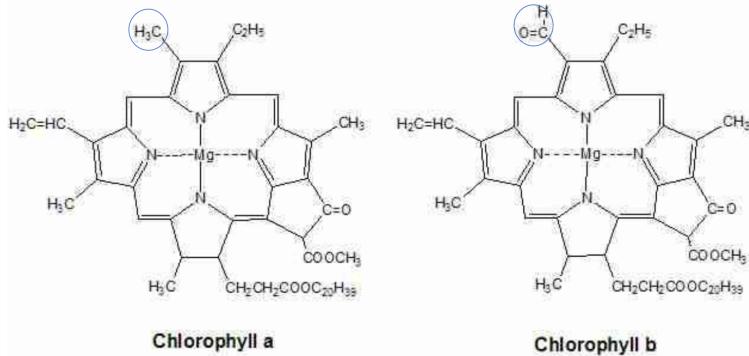


Figure 12: Schematic of Chlorophyll a and b

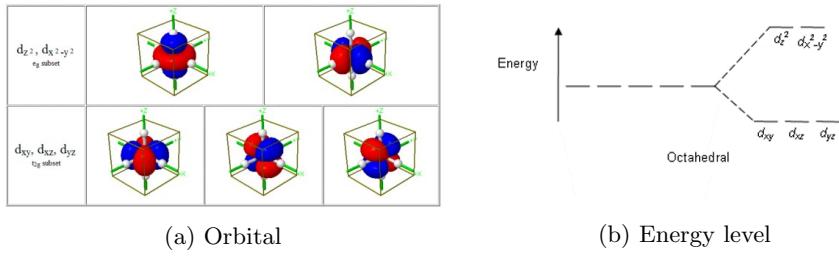


Figure 13: Schematic illustration of d orbital and its energy level

Both chlorophyll a and b has strong absorption for red and blue light, thus only green was left.

### 2.2.1 Color of ions

In the transition metal ion, if it forms a complex with ligands (they sit in octahedrally symmetry sites), as shown in figure 13, there are two scenario: the ligands point between the orbital, or ligands pointing alone the orbital. It turns out that if the ligands are pointing alone the orbital, then it has higher energy (the ligands are -ve charged, they don't like electron cloud).

**N.B.** different ligand splits the energy level differently. If the energy level is small enough, electrons are willing to stay at higher energy level(because it cost energy to pair electrons, the pairing energy is even bigger than the difference in energy level), this result in a high spin state(but optically they are still the same).

**Theorem 2.1.** Beer-Lambert law was illustrated in the equation below.

$$A = \log_{10} \left( \frac{I_0}{I} \right) = \log(\%T^{-1}) = \varepsilon lc$$

Where  $A$  is the absorbence;  $\%T$  is the percentage transmittance,  $\varepsilon$  is a material property, like extinction coefficient,  $l$  is the length of the column,  $c$  is the concentration of the molecule.

The physics version of Beer-Lambert law is

$$\ln\left(\frac{I}{I_0}\right) = -\alpha l$$

Where  $\alpha$  is the extinction coefficient, note  $\ln$  was used instead of  $\log$ , because physicist have different convention to chemists.

### 2.2.2 The color of long molecules

To understand the color of long molecules, we will use the *Particle in a box* Schrodinger equation. It is explained in MSE-105 Quantum Mechanics, so we will just do a quick recap without doing rigorously.

$$\Psi_k(0) = \Psi_k(L) = 0 \quad (2.1)$$

$$V = 0 \quad 0 < x < L \quad (2.2)$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (2.3)$$

The solution is shown in equation 2.4.

$$\psi = C \sin kx + D \cos kx \quad (2.4)$$

Since  $\frac{d^2\psi}{dx^2} = -k^2\psi$ , insert it to the Schrodinger's equation, we get the relation shown in equation 2.5

$$E = \frac{\hbar^2 k^2}{2m} \quad (2.5)$$

Now apply the boundary condition,  $\psi(0) = 0 \Rightarrow D = 0$  and  $\psi(L) = 0$  implies that

$$k = \frac{\pi n}{L} \quad (2.6)$$

Substitute into equation 2.5, we get

$$E = \frac{n^2 \hbar^2}{8mL^2} \quad (2.7)$$

We will now look at why this assumption is valid. Consider figure 14, the electrons in the central chain are *delocalised* because there are a lot of  $\pi$ -bonds. Electrons are free to move in the central chain, but they are not allowed to move past the end of chain.

We will now look at the gap between energy levels. Using equation 2.7, and consider the energy level of  $n$  (LUMO) and  $n+1$  (HOMO), the energy difference is

$$\Delta E = E_{LUMO} - E_{HOMO} = h\nu \quad (2.8)$$

$$\Delta E = \frac{\hbar^2}{8mL^2} [(n+1)^2 - n^2] = \frac{\hbar^2(2n+1)}{8mL^2} \quad (2.9)$$

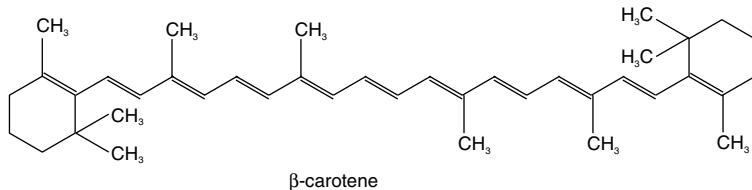


Figure 14: Schematic of a carotene molecule

In the case shown in figure 14, length=30A, and there are 11  $\pi$  bonds, thus n=11, the calculated  $\lambda$  is 1290, it is not visible, but it is just an approximation.

For a charge transfer complex, shown in figure 15, if you shine light onto it, a redox reaction will take place, electron will go from Fe to Co through the C-N bond to Fe. Fe and Co can donate and accept electrons because they *have multiple oxidation state*. This complex has very high extinction coefficient, thus it will produce an intense color.

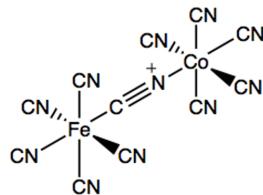


Figure 15: Charge transfer complex

### 2.2.3 Fluorescence and phosphorescence

Note that molecule not only have different energy state, it also have different vibration state. Horizontal line in figure 16 represent different vibration state for molecules. Light move electron up in energy. The LUMO is the the bottom of S<sub>1</sub>, with lowest vibration state. In the excited state, the curve move shifts to the right, because the bond are weaker and further apart from the nucleus. Any optical transition should be *vertical*. It has to go to a state higher than LUMO. Once goto the excited state, it relax thermally back to LuMO. Then again it will drop again to a state(not the lowest vibration state), and relax thermally back to the ground state.

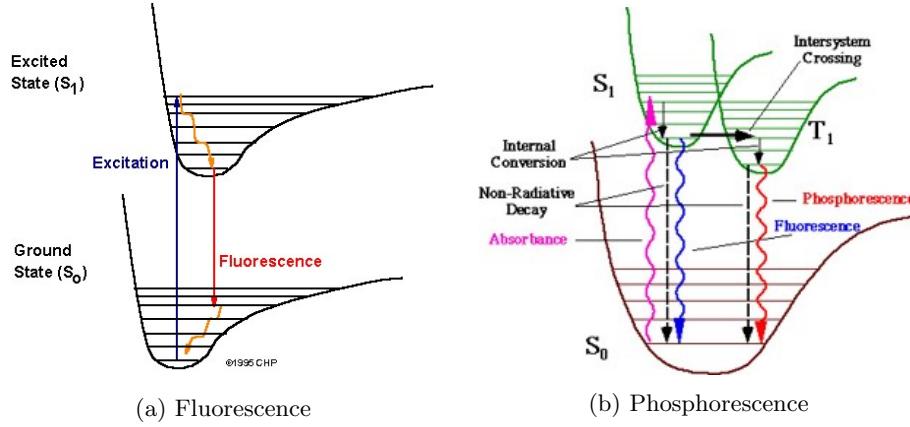


Figure 16: Fluorescence and Phosphorescence

Light can change the angular momentum by 1, but it cannot change the spin state of electron. Without excitation, two electrons in the ground state possess spin of up and down, with spin of +1 and -1 respectively, note that the total spin in a system is  $2s+1$ , after excitation, the excited electron thus has opposite spin to the other electron in ground state of  $S_0$ . In both cases, the total spin is 1, it is a singlet state. In phosphorescence, again light causes the electron to move vertically up, it thermally relax to the lowest state in  $S_1$ . then it will go to  $T_1$  (this process is called intersystem crossing), where its spin fliped, it is called triplet now because both spin are +1, and  $2s+1 = 2$ . But it cannot come back to  $S_0$  again easily due to pauli's exclusion principle, it go to  $S_0$  ground by a very complex and rare mechanism. It takes hours or days for electron to come back.

### 2.3 Color of insulators

An insulator is a material the band gap correspond to a UV light. ZnO is a material that is almost insulator, i.e. it has a band gap that just absorb a small fraction of very high frequency visible light. From what we have learned previously, in an insulator, only the light with  $\frac{hc}{\lambda} > E_g$  can be absorbed. However, as we look at the real absorption spectra, we observe some peaks *before*  $E_g$ , it turns out that they arise from *excitons*.

**Definition 2.1.** An *exciton* is a bind electron hole pair.

Consider the electrons, it is *bind* to the hole, it is not free to move, thus it has slightly *lower* energy as if it is in CB, and free to move. So we can observe some energy state just below CB. These are illustrated in figure 17. For a photon that can excite the electron into the exciton energy level, it fulfill equation 2.10. Where  $E_B$  is the binding energy. In fact, there are multiple states shown in figure 17, because there are multiple states in it.

$$h\nu = E_g - E_B \quad (2.10)$$

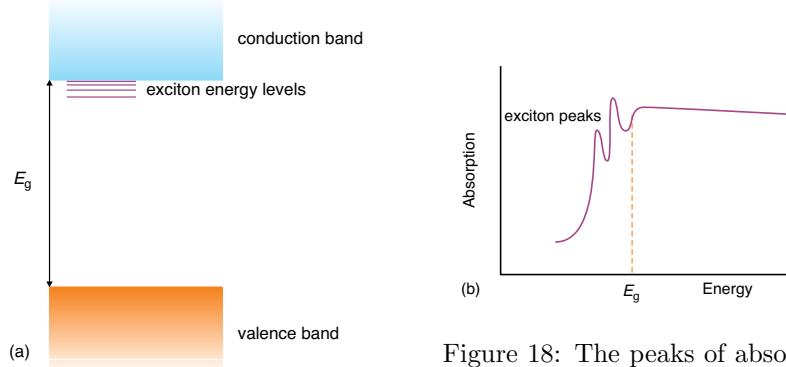


Figure 17: The energy level of excitons

Figure 18: The peaks of absorption spectra at  $kT < E_B$ .

**Definition 2.2.** In a *Mott-Wannier* exciton, electron and holes are loosely bonded. It generally occurs in material with large dielectric constant.

**Definition 2.3.** In a *Frenkel exciton*, electrons are tightly bonded by the holes(in fact bind to atom). In fact it is so tightly bonded that it is just outmost electron excited to its closest state. e.g. from  $1s^22s^22p^6$  to  $1s^22s^22p^53s^1$ . It occurs in materials with small dielectric constant.

We will now look at how to color the insulator. First, a typical example was introduced in MSE-105 Thermodynamics of defects. If you expose *alkali-halide*, like NaCl to x-ray, it will get colored.

**Definition 2.4.** A *color centre* in a Face center material was produced if an face centered anion was removed, and left behind an electron. The electron has multiple states as it surround these cations. And the energy difference between states correspond to visible light.

Apart from that, we can also create color by *doping impurities to an insulator*.

**Example 2.3.1.** In Al<sub>2</sub>O<sub>3</sub>, if we dope some  $Cr^{3+}$ , it will become a ruby, which is *red*. This is because as  $Cr^{3+}$  has outmost electron in an unfilled d-orbital, as it replace Al<sup>3+</sup>, it will be surrounded by a octahedral environment, which cause d-orbital to split, the energy difference between these d-orbital correspond to red light.

Now we will look at some application of color insulating material.

**Example 2.3.2.** In the old days, the display screen was designed in a following manor. We use a hot cathode to generate electron, after electron pass through

the anode, it will be focused in a focal coil, deflected by the deflecting coil and hit a fluorescent screen, the screen become colored as electron hitted. This is because screen contains phosphorous.

What is the material requirement of this cathode? Let's look at equation 2.11 for the thermionic emission.

$$j_c = AT^2 \exp\left(-\frac{\Phi}{kT}\right) \quad (2.11)$$

$$A = \frac{4\pi mk^2 e}{h^3} \quad (2.12)$$

Where  $A$  shown in equation 2.12 is the Richardson constant, it has a magnitude of  $1.2 \times 10^6 Am^{-2} K^{-2}$ . To *maximise*  $j_c$ , we have to use high T, and a material with low work function  $\Phi$ . A typical example is CsO. But this design is not as good as the television nowadays. We will look at some improved version.

**Example 2.3.3.** In a plasma screen, as illustrated in figure 22 it has a lot of boxes above and below which there are electrodes. In each sub-pixel, it contains low pressure gas that give rise to plasma. As you apply a voltage in both top and bottom electrode, the electron of the plasma collide with the phosphors, and light was emitted. Each box represents a sub-pixel. It can emit one of RGB. The problem with this design is that it we have to put gas in to *a lot of boxes*, each isolated and sealed, they cannot leak.

**Example 2.3.4.** Since there are issues with the previous two design, we will look at the best design 5 years ago. This design is called *Select electron diodes* or SEDs. They are individual addressable cathodes. This is illustrated schematically in figure 20. We can find that SEDs contains a lot of individually addressable cathodes, i.e. you can switch each cathode on and off, they are *carbon nanotubes*. They can be inserted by putting an array of carbon nanotube on the screen, and they can be forced to pointed upward by putting a tape on it, and pull it. The current is given by

$$j = AE^2 \exp\left(-\frac{4\pi\Phi^{3/2}}{3E}\right)$$

It is strongly *field dependent*. A high field can be achieved by using high voltage / *low distance*. We can make the nanotube same length by running it for 10 minutes, this is because for long cathode tube, it has low distance to the screen, thus high field and *very high current*. The high current cause the tube to burn. Until it is the same length as the others.

### 2.3.1 Making each color

To make the blue and green color, let's look at the luminescence excitation mechanism:

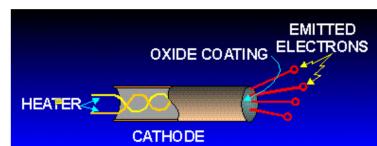


Figure 19: This is a hot cathode

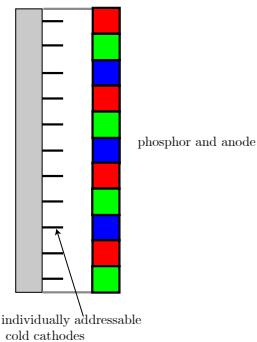


Figure 20: This is an SEDs

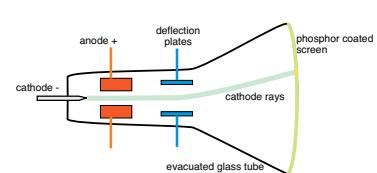


Figure 21: Caption

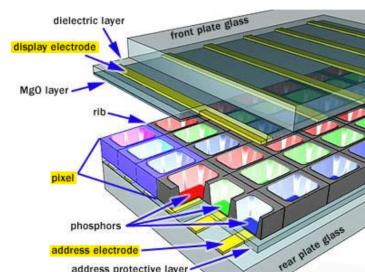


Figure 22: This is a plasma screen

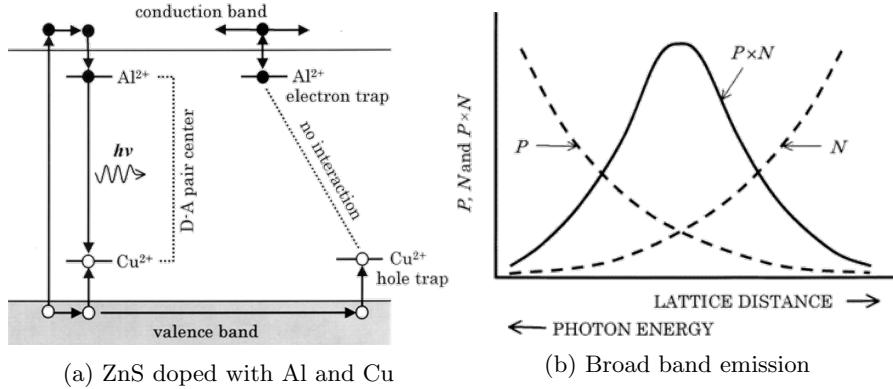


Figure 23

First, the phosphor was collided directly to the primary electron. Plasmon excitation take place. Next charge was transferred between the activator and host lattice. Finally, electrons and hole pair was recombined at the luminescence center.

For blue and green, we used ZnS, the VB is purely S2-, and CB is Zn2+. If you add impurities, such as Al, Cu. Al is an acceptor, and Cu is a donor.(fig 23a) Al accept an electron from the CB, and Cu accept a hole from VB. The separation between donor and acceptor correspond to visible spectrum. Note Al is a acceptor to the CB, that is why it is a acceptor. But the donor and acceptor need to be close enough to interact, in fact this gives us broad band emission. The energy of the emission is

$$E(r) = E_g - (E_D + E_A) - \frac{e^2}{4\pi\epsilon r} \quad (2.13)$$

Where  $E_D$  and  $E_A$  are the distance from the donor/acceptor level to the VB/CB. The last term is the columbic interaction between the electron/hole when they come close together before recombination. So essentially you can get a wide range of possible energy. However, as i increase  $r$ , the distance between electron and hole are high, they are unlikely to recombine. However, if  $r$  is too small, there is low probability of finding a e.g. accepter and donor pair is low. This is why overall, you get this dumbbell shaped emission spectrum. (fig:23b)

To get red light, you have to use rare earth material as the base material, in fact these material get atomically sharp lines, but we have a lot of peaks, and they are close together.

To form the film, you have to mix some phosphor, PVA and ammonium dichromate, spin coat it in a substrate material. Then you do some photolithography, the mixture will crystallise when the light was shine. As shown in figure 24.

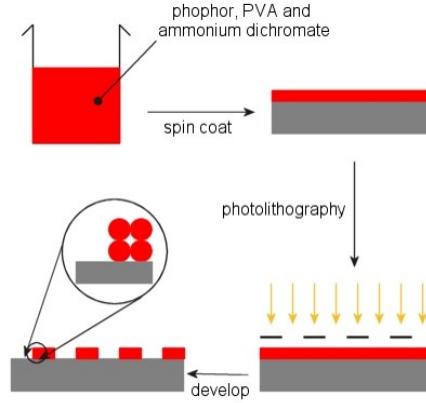


Figure 24: Caption

## 2.4 Color of semiconductor and metals

In a semiconductor it has a band gap correspond to visible light, all the wave with  $\lambda < \frac{hc}{E_g}$  will get absorbed. the rest will get transmitted or reflected. This is the color of the semiconductor.

Now we will do a little bit to revision for MSE-205 Quantum theory of materials. Consider equation 2.7, for a semiconductor,  $L$  is very big, so we will get a parabolic  $E-n$  relation, but with almost no gap in it. As shown in figure 25. However, if we put some atoms inside, it become a little different. We can still treat  $V \approx 0$ , but as shown in figure 26. The waves should have same energy because they have same frequency, but they don't because the red wave has a maximum near the atoms, thus the energy is lower compare with blue, where it has a minimum at the atom. The  $E_g$  arise from this curve split. As shown in figure 27. However, we are living in 3D, the atomic spacing is different from one direction to another, as shown in figure 28. It turns out that the minimum CB might not lie on top of the VB top. As shown in figure 29.

**Definition 2.5.** An *Indirect* semiconductor is one with CB bottom and VB top do not lie on the same position in k-space.

**Definition 2.6.** An *direct* semiconductor is one with CB bottom and VB top do lie on the same position in k-space.

The momentum of the photon is negligible. If we want to excite an electron in an *indirect* semiconductor, we not only need to change its energy(by use of photon), but also need to change the direction(and momentum) it is travelling(by phonon). Thus, *We need to couple an electron, photon and phonon in the same place to excite an electron.* This is a rare event.

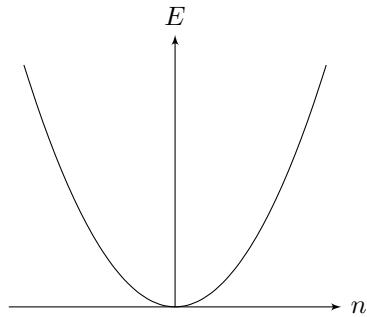


Figure 25: The energy level of electron in a very large box.

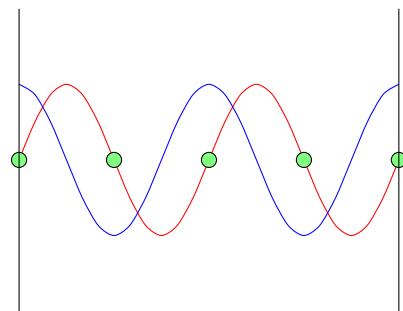


Figure 26: Two waves that have same E at PIB model

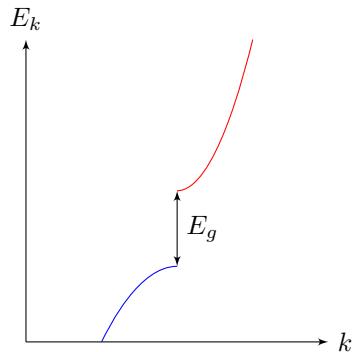


Figure 27: Caption

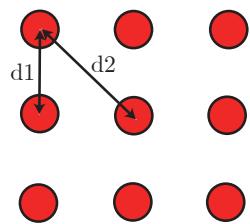


Figure 28: The atomic distance in the diagonal direction and the horizontal direction

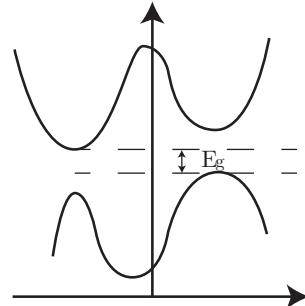
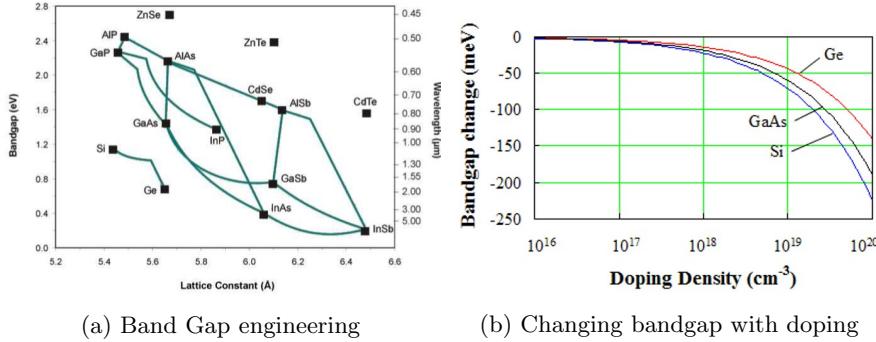


Figure 29: Schematic of an indirect semiconductor.



**Theorem 2.2** (Beer-lambert law). In a solid, the Beer-lambert law is given by.

$$\ln \frac{I_0}{I} = \alpha l$$

In a solid, we do not have concentration, so it is replaced by  $\alpha$ , the attenuation coefficient.

The consequence of being an indirect semiconductor is that the  $\alpha$  value is significantly lower in certain wavelength. Until the photon energy is so high that it can excite directly to the CB on its top.

#### 2.4.1 Changing the band gap

We can change the band gap of semiconductor by band gap engineering, i can mix the fixed fraction of different material, and tune the band gap we want. For example, for the Al-As-Sb ternary system, as i change the composition, i move alone the line shown in figure 30a. This is because lattice constant changes, thus it changes the wavelength of the light it can absorb. There are some equation to calculate the band gap. Thus, by making ternary, you can change the band gap.

Apart from that, the band gap changes with the concentration of dopants. It decreases, this is because the impurity levels overlap with the VB/CB, you made *bands* with high concentration of dopants.

Transparent conducting oxide (TCO) is an very important material for electronic device, it is  $\text{In}_2\text{O}_3$ , doped with 5-15%  $\text{SnO}_2$ . It is behaving like a metal, it can conduct electricity, but it is *transparent*. Essentially we use an insulator as a base material, which makes it transparent, but we dope too much, the dopants form their own bands, giving rise to conduction.

**Example 2.4.1.** In a *Photoconductive detectors*, as light shine onto it, the electrons in the VB will be promoted to the CB, there are more free charge carriers, so resistance decrease. We will derive some important equation for this device. First, we will calculate the number of photon incident onto the surface, this is equal to

$$\text{no. of Incident photon} = \frac{I_0 WL}{h\nu} \quad (2.14)$$

Where  $W \times L$  is the area of the device, and  $I_0$  is the intensity. We are just basically dividing the total energy by the energy of one photon. Now the number of photon absorbed are

$$\text{no. of absorbed photon} = \frac{\eta I_0 WL}{h\nu} \quad (2.15)$$

Where  $\eta$  is the efficiency, it accounts for the *fraction* of photon that converted to the electron. Because not all the electron are absorbed. It can be calculated by equation 2.16.

$$\eta = \left[ 1 - \left( \frac{n-1}{n+1} \right)^2 \right] \times [1 - \exp(-\alpha D)] \quad (2.16)$$

Where the  $\left[ 1 - \left( \frac{n-1}{n+1} \right)^2 \right]$  term are correction for *reflection*;  $[1 - \exp(-\alpha D)]$  are just Beer Lambert law. Then we divide it by the volume. And we get  $r_g$ , as shown in equation 2.17

$$r_g = \frac{\eta I_0 WL}{h\nu WLD} = \frac{\eta I_0}{h\nu D} \quad (2.17)$$

Where  $r_g$  is the rate of generation of current. The rate of *recombination* is given by

$$r_r = \frac{\Delta p}{\tau_c} \quad (2.18)$$

Where  $\Delta p$  is extra amount of holes (in a n-type device).  $\tau_c$  is just basically the minority carrier lifetime. Note since it is a n-type device, electrons are in excess, so holes are more important. At equilibrium,  $r_r$ , the rate of recombination is given by  $r_r = r_g$ , then we can deduce that

$$\begin{aligned} \Delta p &= \frac{\tau_c \eta I_0}{h\nu D} \\ \sigma &= ne\mu_e + pe\mu_h \end{aligned}$$

Thus we get

$$\Delta\sigma = \frac{\tau_c \eta I_0 e}{h\nu D} (\mu_e + \mu_h) \quad (2.19)$$

Then we can use the relation between  $\sigma$  and  $i$ (current), as shown in 2.20

$$\Delta i = \frac{WD\Delta\sigma V}{L} \quad (2.20)$$

Then we finally have

$$\Delta i = \frac{\tau_c \eta I_0}{L h\nu} (\mu_e + \mu_h) V \quad (2.21)$$

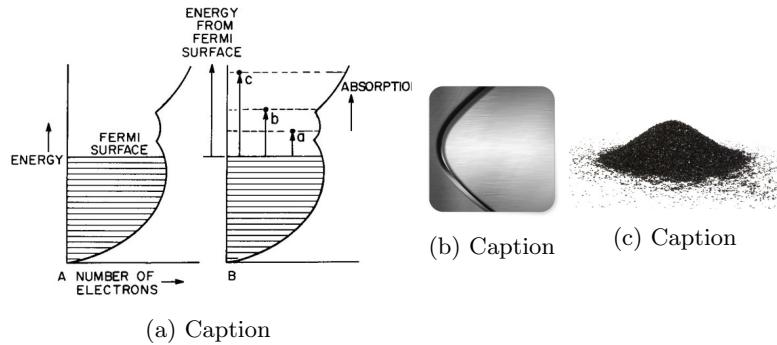


Figure 31

#### 2.4.2 Color of metals

In a metal, since the spacing between energy levels are too small, almost any transition is allowed. But once the light was absorbed, it will re-emit immediately. So you get 100% reflectivity. Unless you have d band. But for powders, it will scatter the light, thus for ZnO appears white, in metal, the light stucked in all the total internal reflections, thus they appears black.

### 3 Introduction to liquid crystal

#### 3.1 Basic terminology

**Definition 3.1** (Nematic phase). A nematic phase has position disorder, and *orientation order*. As shown in figure 32

**Definition 3.2** (Director). A director  $\mathbf{n}$  is the preferred orientation of crystal.

This phase is very unstable, it exist only at a narrow range of temperature. And the  $\Delta H = 5J/g$ . We just need a small amount of energy to destroy this orientation order. The next problem is how can we define quantify the orientation order? Because some might just orientate slightly towards the director, while others align exactly at the director. To quantify the orientation, we introduced the parameter  $S$ . Which can be calculated in equation 3.1. Note  $\langle \rangle$  means take average.

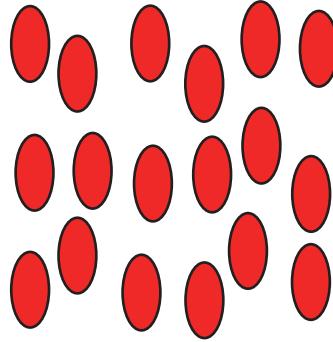


Figure 32: Nematic phase

$$S = \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle \quad (3.1)$$

**Definition 3.3** ( $T_c$ ).  $T_c$  is the temperature where the nematic phase transform to a liquid phase.

As temperature increase, the  $S$  value decrease, when pass through  $T_c$ ,  $S$  drop discontinuously to 0. This indicate a phase transition. And the material will become isotropic.

Another important phase is the *Smectic phase*, it is defined as follows.

**Definition 3.4** (Smectic). A smectic phase is a liquid crystal with some orientation order and some *position order*.

In a smectic phase, the molecules are *stacked in layers*. The layers can slide over each other, but molecule are still sitting in layers.

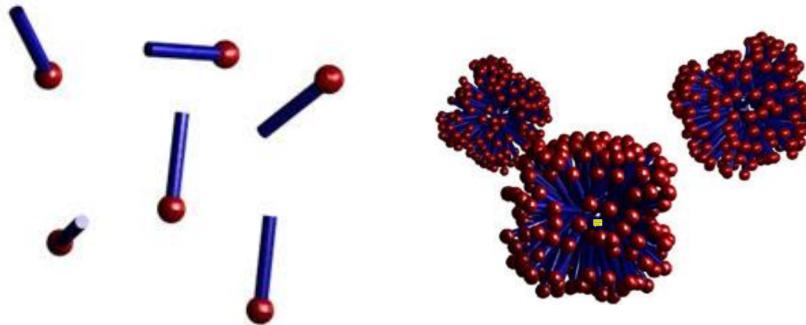


Figure 34: micelles

Figure 33: Individual molecule

**Definition 3.5** (Smectic A). In a Smectic A phase, the director is *parallel* to the plane normal of layers.

**Definition 3.6** (Smectic C). In a Smectic C phase, the director has an angle to the layer's normal.

As we heat up the liquid crystal, we will always undergo phase transition, and the phase transition is such that the order is destroyed. This prohibit some pathway of phase transition. e.g. we can also go from Solid  $\rightarrow$  Smectic  $\rightarrow$  Nematic  $\rightarrow$  Liquid, we can also go from Nematic phase directly to liquid phase(you can miss step),. But we cannot go from Nematic to Sematic.

**Remark.** The requirement for liquid crystal is they are strongly polar molecule. (most have rod shape but this is less important).

I will  $\text{\LaTeX}$ the common molecule later.

Now we will consider what if a mesophase is in solution. In very dilute solution, the individual molecules are separated. As shown in figure 33, then as the concentration increase, it form micelles, a clump of chains. The tail(hydrophobic) will point in and head (hydrophilic) point out. This is useful because tails dissolve oils, and secrete it inside the micelle. As concentration increase further, it will transform in micelles  $\rightarrow$  hexagonal  $\rightarrow$  lamellar. The structure was shown in figure 33, 34, 35, 36. There are some special property of the viscosity of liquid crystal. i.e. since they arrange in planes, there is some easy shear direction, some more difficult directions. It turns out that if force is parallel to  $\mathbf{n}$ , then viscosity is lowest, while if we shear in a plane perpendicular to  $\mathbf{n}$ (because all rods are pointing upward), the viscosity is higher. This is illustrated in figure 37. Note that as we increase T above  $T_c$ , then the viscosity become isotropic.

The spacing between liquid crystals are order of molecule size. As a result, it will scatter x ray in a very small angle.

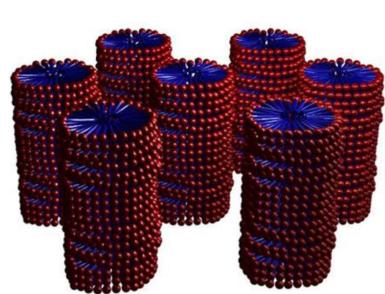


Figure 35: hexagonal

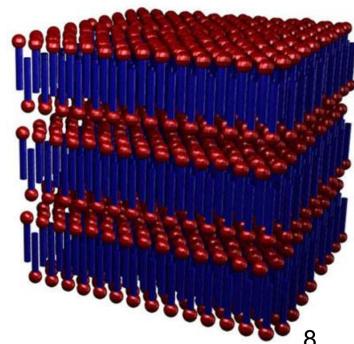


Figure 36: lamella

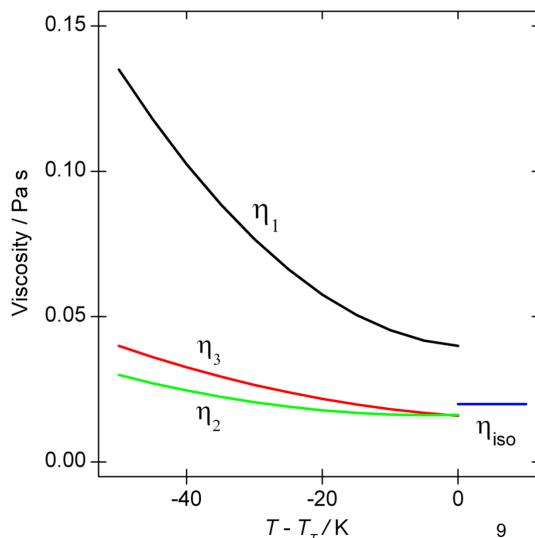
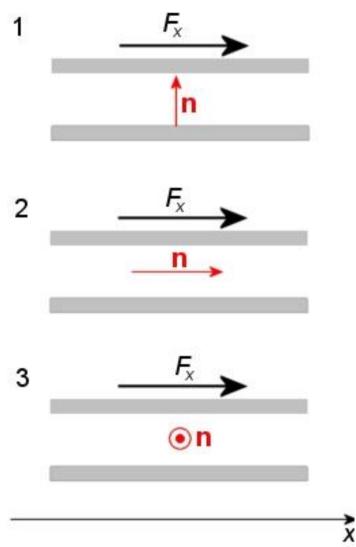


Figure 37: Caption

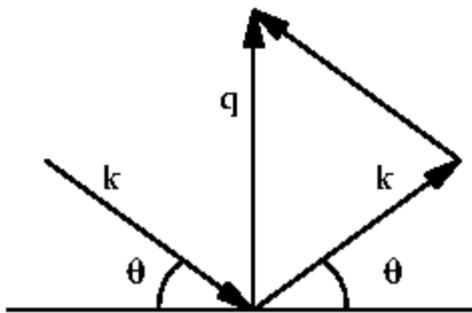


Figure 38: Caption

**Definition 3.7** (SAXS). SAXS stands for *small angle x-ray scattering*. It uses X-ray of multiple wavelength, and very long distance between sample and detector.

Since it is multiple wavelength, it is difficult to work out bragg's law for each individual wavelength, we instead use  $q$ . which is shown in figure 38. The derivation is follow.

$$\begin{aligned} n\lambda &= L \sin(2\theta) \\ n\lambda &\approx 2L \sin \theta \\ n \frac{2\pi}{L} &\approx \frac{4\pi}{\lambda} \sin \theta = q \end{aligned}$$

Note  $q$  is defiend as

$$q = \frac{4\pi}{\lambda} \sin \theta \quad (3.2)$$

The SAXS result was shown in figure 39. For isotropic one, a ring was observed. For nematic phase, there are a peak at the horizontal axis, this is because the all the molecule are aligned in the vertical direction, so the x ray continuously see the short spacing, giving these feature. For sematic A, there are repeated pattern in horizontal and vertical direction, thus a peak is observed in the horizontal and vertical axis. For the Sematic C the short and long image are not orthogonal. they are at an angle of  $90 - \theta$  relative to each other. By doing the SAXS, you can know the angle between the director and the plane normal. **N.B.** a longer distance in the crystal will produce a shorter shade in the diffraction pattern.

In a chiral molecule, there are two enantiomers which is mirror image of each other, they will rotate light differently. You can rotate molecule 1 and 2, but they cannot impinge each other.

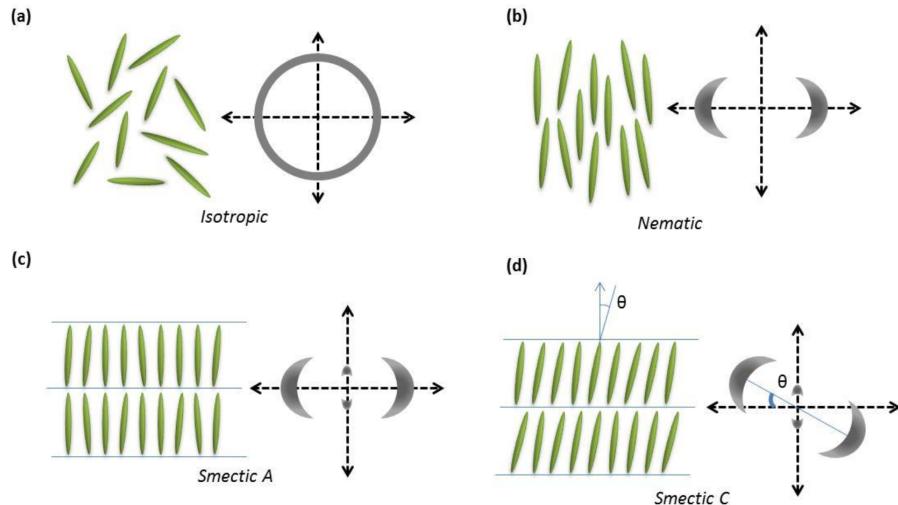
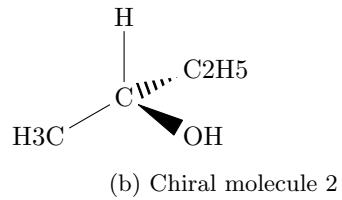
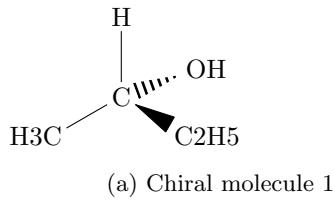


Figure 39: Caption



In a chiral nematic phase, within a layer, all the molecules are oriented in one direction(directrix), but there is a slight twist between each layers. As i go up the layer, the director was rotating around. The repeat length  $l$  defines the length for the molecules to turn 180 degrees(so that the molecules adapt the same orientation), the pitch length  $p$  define the length for them to turn 360 degrees.  $l$  is 300-800 nm, correspond to wavelength of light. Note that  $l$  is temperature dependent.

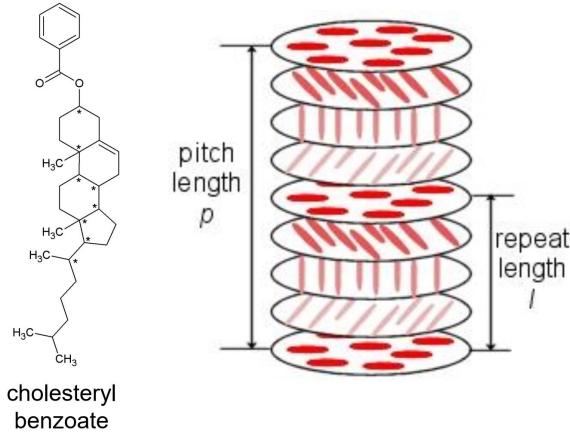


Figure 41: Schematic illustration of a typical chiral molecule, with each star corresponding to a chiral center. And the crystal orientation in each layer of a chiral nematic phase.

In the chiral smectic phase, the 'direction' of the molecules are rotating around a cone. **N.B.** the overall spontaneous polarisation is 0, but a single layer is a ferroelectric.

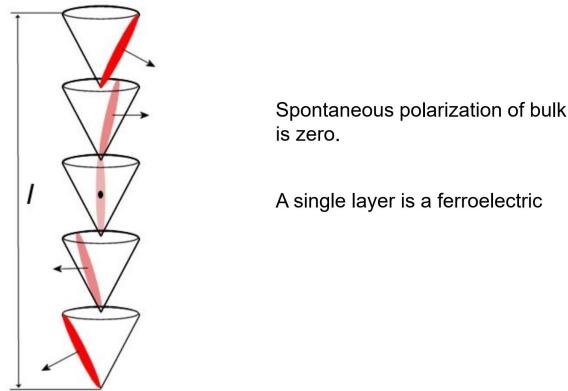


Figure 42: Caption

### 3.2 Polarisation of light

From section 1, a linear polarised light has formula of

$$E_x(z, t) = E_{0x} \cos(kz - \omega t)$$

$$E_x(z, t) = E_{0y} \cos(kz - \omega t)$$

However, in many case, the x component and y component has a phase shift, this can be formulated by

$$E_x(z, t) = E_{0x} \cos(kz - \omega t) \quad (3.3)$$

$$E_y(z, t) = E_{0y} \cos(kz - \omega t + \delta) \quad (3.4)$$

**Definition 3.8** (Circular polarised). In a circular polarised light,  $\delta = \pm\pi/2$ . For the wave formulated in equation 3.3 and 3.4, Both of them are travelling in the z direction, but the  $\theta = \pi/2$  one will clockscrew in the clockwise direction, the  $\theta = -\pi/2$  one will clockscrew in the anticlockwise direction. As illustrated in figure 43.

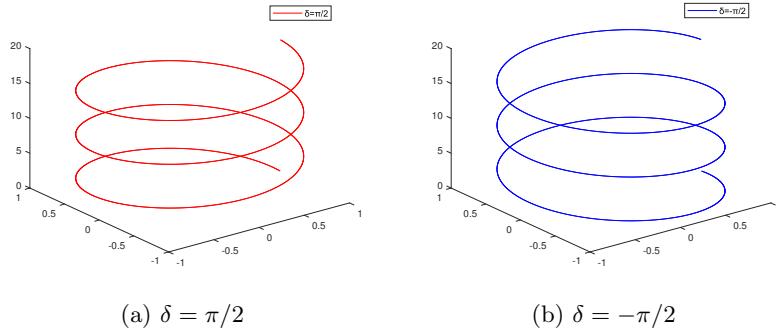


Figure 43

**Definition 3.9** (Eclipsed polarised). In majority of time, if either  $E_{0x} \neq E_{0y}$  or  $\delta \neq \pm\pi/2$ , then the wave is travelling like an eclipse in the x-y plane, it is a *circularly polarised light*.

**Definition 3.10** (Refractive index). The refractive index of the wave  $n$  is given by  $n = \frac{\lambda_0}{\lambda}$ , the speed of light in a medium is given by  $v = \frac{c}{n}$

**Definition 3.11** (Birefringence). The  $n$  value in some material is not isotropic, it is different in different direction. This phenomenon is called *birefringence*.

e.g. Most polymer are birefringent, because the polymer are pulled to all align in one direction. Since they are all aligned, the polymer has different dipole moment in different direction, thus different  $n$ .

In the liquid crystal, there are 2  $n$ 's, ordinary and extraordinary.

**Definition 3.12** (ordinary). The R.I. in the ordinary axis  $n_o$  correspond to the R.I. perpendicular to the directrix

**Definition 3.13** (Extraordinary). The R.I. in the extraordinary axis  $n_e$  correspond to the R.I. parallel to the directrix

Note that extraordinary often has a higher value, the difference between these two are given by equation 3.5. According to figure 44, at very high temperature, it is no longer liquid crystal and the material only has one  $n$ .

$$\Delta n = n_e - n_o \quad (3.5)$$

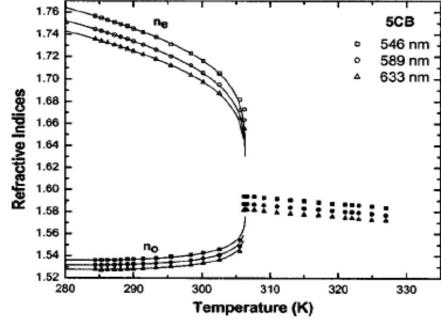
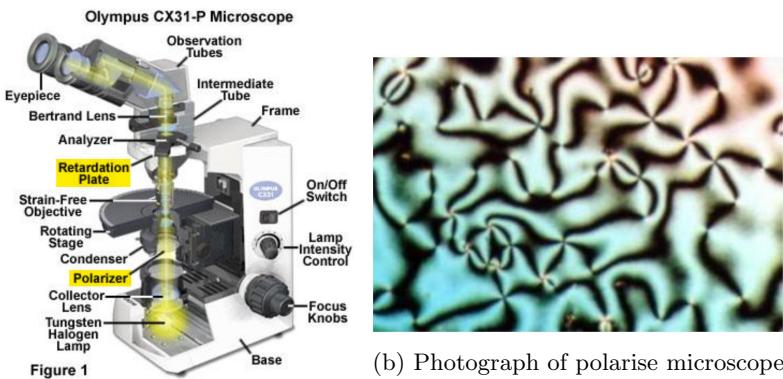


Figure 44: Caption

To observe the nematic phase, we can use the polarising microscope, as seen in figure 45a. It is similar to normal microscope, but it has two perpendicular plates. In one plate, it only allows the light traversing in the e.g. horizontal direction to pass. But the direction of the other lens is vertical, hence in normal condition, no light will get through. However, birefringent twist the light, so light will pass through.



(a) Polarising microscope

Figure 45

But in figure 45b, we can see some of the dark in the figure, this is due to the presence of defects. The defect cause liquid crystal to align in specific

ways. as shown in figure 46. If the direction of polarisation is either *parallel or perpendicular* to the alignment of the polymer, the light is only feeling one  $n$ , thus it remain linearly polarised without changing its direction of polarisation. Hence it will appear dark.

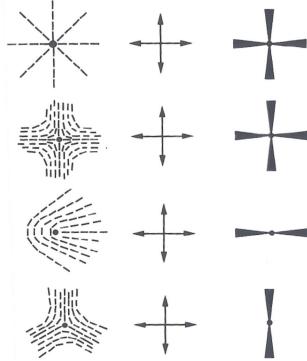


Figure 46: Caption

Now we will try and formulate the twisting of light. Consider a light polarising  $45^\circ$  to the directrix, as shown in figure 47

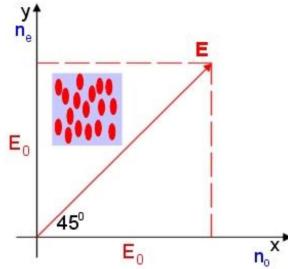


Figure 47: Caption

before entering the liquid crystal, the field is given by

$$E_x(z, t) = E_{0x} \cos(k_0 z - \omega t)$$

$$E_y(z, t) = E_{0y} \cos(k_0 z - \omega t)$$

After entering the LC, ( $z \in [0, d]$ ,  $d$  is the thickness of the LC) the light in these direction is given by

$$E_x(z, t) = E_{0x} \cos(n_o k_0 z - \omega t) \quad (3.6)$$

$$E_y(z, t) = E_{0y} \cos(n_e k_0 z - \omega t) \quad (3.7)$$

After leaving the LC( $n = d$ ), We can reformulate using  $\Delta n$  it and just consider the phase shift.

$$E_x(z, t) = E_{0x} \cos(n_o k_0 d - \omega t) \quad (3.8)$$

$$E_y(z, t) = E_{0y} \cos(n_o k_0 d - \omega t + \Delta n k_0 d) \quad (3.9)$$

The phase shift is then given by  $\delta = \Delta n k_0 d$ . (Usually it cause the light to be eclipsely polarised).

**N.B.** We can design the material such that  $\Delta n k_0 d = \pi/2$ , so it produce the circularly polarised light. We can also design such that  $\Delta n k_0 d = -\pi$ . Then the transmitted light is linearly polarised, but the direction of polarisation is perpendicular to the incident one.

Now let's consider how the light behaves as we put the light in a chiral nematic phase. Note that the director is changing over space. As shown in figure 48a.

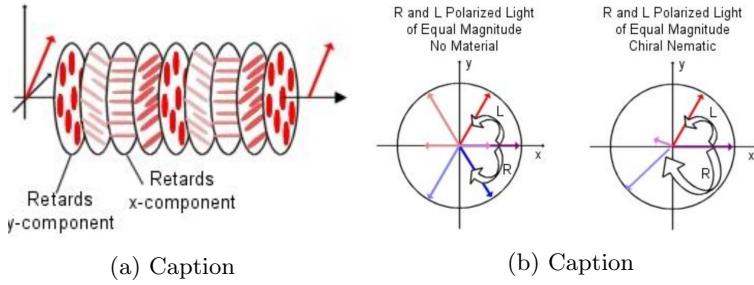


Figure 48

We also require these two condition, the first one is to say the distance between success plates are small.

$$P < 50\lambda \quad (3.10)$$

$$P \neq n\lambda \quad (3.11)$$

Another way to think about the linearly polarised light is to think like the sum of two circularly polarised light. As shown in figure 48b. When there is no material, the x direction of oscillation add, y direction of oscillation cancel, thus the net oscillation is like a linear polarised light. However, in the chiral nematic, one direction is rotation is the same as the direction of director rotation, this one will rotate faster than the one, where rotate against director's rotation. The net result is the direction of oscillation changes.

Now we will do the math of this system. Consider figure 49a. Note that this time the light coming is not  $45^\circ$  with the x and y direction, but it is making an angle  $\phi$  with the directrix.

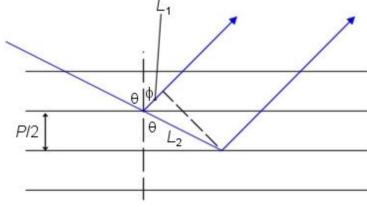


Figure 50: Caption

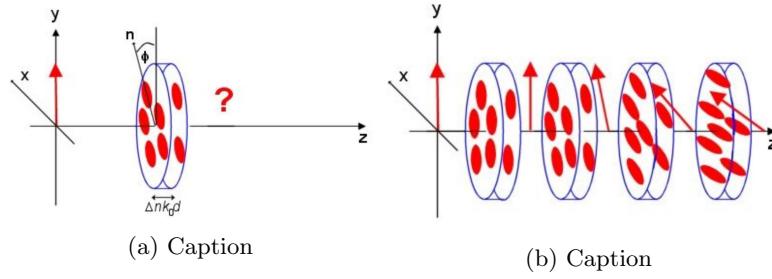


Figure 49

$$E_x(z, t) = E_0 \cos(\phi) \cos(n_o k_0 d - \omega t) \quad (3.12)$$

$$E_y(z, t) = E_0 \sin(\phi) \cos(n_o k_0 d - \omega t + \Delta n k_0 d) \quad (3.13)$$

Note that  $\Delta n k_0 d \approx 0$ , as this layer is only one molecule thick. The angle of light coming out is given by

$$\theta = \arctan \left( \frac{\cos \phi}{\sin \phi} \right) = \frac{\pi}{2} - \phi \quad (3.14)$$

What this means is that the light coming out is oscillating along the director. This can be seen in figure 49b.

Now we will do some bragg's law to these liquid crystal. Consider figure 50, The path difference between the top light and the bottom light is given by equation 3.15, but this should equal to  $n\lambda$ , thus we can deduce equation 3.16.

$$n\lambda = L_2 - L_1 = \frac{P}{2 \cos \theta} [1 + \cos(\theta + \phi)] \quad (3.15)$$

$$n\lambda = \frac{P}{2 \cos \theta} [1 + \cos(\theta + \phi)] \quad (3.16)$$

If  $\theta = \phi$ , equation 3.16 becomes

$$n\lambda = P \cos \theta \quad (3.17)$$

This is selective reflection, it will only reflect visible light of certain wavelength. Note  $P$  depends on temperature, thus we can build a cheap thermometer based on this phenomenon. (High temperature cause the LC to reflect light of a different wavelength )

### 3.3 Liquid crystal and fields

Consider a two plates in vacuum, the charge stored in the plate of is given by

$$\frac{Q_0}{A} = \epsilon_0 E \quad (3.18)$$

Note that  $E$  is the electric field *generated from battery*, it is a *scalar*. However, as we put a medium between the plates (with same cross sectional area  $A$ ), then the medium will get polarised. the dipole per unit volume is given by

$$P = \epsilon_0 \chi E \quad (3.19)$$

Where  $\chi$  is the susceptibility of the material, which is dimensionless.

**Definition 3.14** (Displacement). The displacement of a material  $\mathbf{D}$  is given by

$$\mathbf{D} = \epsilon_0 E + \epsilon_0 \chi \mathbf{E} \quad (3.20)$$

Now, we will calculate the work done in putting the charge in the capacitor. The circuit was illustrated in figure 51.

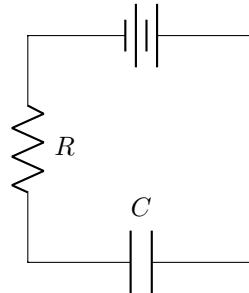


Figure 51: Caption

For adding 1 charge  $q$ , the work done  $du$  is given by

$$du = V_c dq \quad (3.21)$$

Where  $V_c = \frac{q}{C}$  is the potential difference across the capacitor (cause some  $V$  was absorbed by the resistor). By integration, we get

$$\int_0^{u_f} du = \int_0^{Q_f} \frac{q}{C} dq \quad (3.22)$$

$$u_f = \frac{1}{2} \frac{Q_f^2}{C} \quad (3.23)$$

Where  $f$  indicate final. At this stage, there is no current, so no potential accross the resistor, thus  $V_c = V = \frac{Q_f}{C}$ . We can conclude that

$$u_f = \frac{1}{2} Q_f V \quad (3.24)$$

Now we will calculate the work done per unit volume  $U_f$ , this can be done by dividing  $u_f$  by distance and area.

$$U_f = \frac{1}{2} \frac{V}{d} \frac{Q}{A} \quad (3.25)$$

We know that  $E = \frac{V}{d}$  and  $\frac{Q}{A} = D$ , thus we get

$$U_f = \frac{1}{2} \mathbf{E} \mathbf{D} \quad (3.26)$$

But liquid crystal is anisotropic, what it means is that  $\chi$  is a 2<sup>nd</sup> rank tensor. Thus the relation between  $\mathbf{P}$  and  $\mathbf{E}$  is given by

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E} \quad (3.27)$$

$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} \chi_o & 0 & 0 \\ 0 & \chi_o & 0 \\ 0 & 0 & \chi_e \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \quad (3.28)$$

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = \epsilon_0 (1 + \chi) \mathbf{E} \quad (3.29)$$

What one can also do is to split  $E$  and  $P$  into two parts, one ordinary part, and one extraordinary part.

$$\mathbf{P}_e = \epsilon_0 \chi_e \mathbf{E}_e \quad (3.30)$$

$$\mathbf{P}_o = \epsilon_0 \chi_o \mathbf{E}_o \quad (3.31)$$

$$(3.32)$$

If  $\mathbf{E}$  is not parallel to  $\hat{\mathbf{n}}$ , we can also Gram-Schmidt method to find the magnitude ordinary and extraordinary part.

$$E_e = \mathbf{E} \cdot \hat{\mathbf{n}} \quad (3.33)$$

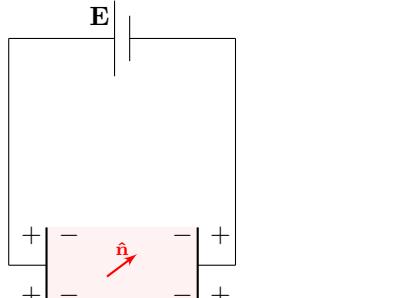
$$E_o = |\mathbf{E} - (\mathbf{E} \cdot \hat{\mathbf{n}})\hat{\mathbf{n}}| \quad (3.34)$$

The polarisation is given by

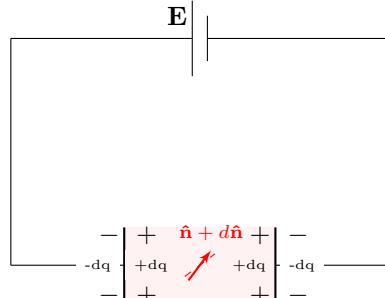
$$\mathbf{P} = \epsilon_0 [\chi_o \mathbf{E} + \Delta \chi (n \cdot \mathbf{E}) \hat{\mathbf{n}}] \quad (3.35)$$

Where  $\delta\chi$  is the differnece in  $\chi$  between the ordinary and extraordinary direction.

However, remenber that liquid crystal is a liquid, the molecule will also change its direction of alignment when one apply an electric field, hence  $\hat{\mathbf{n}}$  will change.



(a) Caption



(b) Caption

Figure 52

As shown before, the electronic energy stored in the system is given by

$$U_e = \frac{1}{2} \mathbf{D} \cdot \mathbf{E} \quad (3.36)$$

The change in energy  $dU_{e1}$  due to the change in *director orientation* is given by

$$dU_{e1} = \frac{1}{2} \mathbf{E} \cdot d\mathbf{D} \quad (3.37)$$

To calculate  $d\mathbf{D}$ , consider equation 3.20, if  $\mathbf{E}$  is constant, we can conclude that  $d\mathbf{D} = d\mathbf{P}$ , thus we get

$$dU_{e1} = \frac{1}{2} \mathbf{E} \cdot d\mathbf{D} \quad (3.38)$$

Now we will calculate the energy change in energy  $dU_2$ , it is equal to

$$dU_{e2} = -\frac{Edq}{A} = -Ed\sigma \quad (3.39)$$

Where  $\sigma$  is the surface charge,  $d\sigma$  is equal to the change in electric displacement  $d\mathbf{D}$  perpendicular to the plate, we can calculate the direction of plate normal by  $\hat{\mathbf{n}}_{\text{normal}} = \frac{\mathbf{E}}{E}$ .

$$d\sigma = \frac{\mathbf{E}}{E} \cdot d\mathbf{D} = \frac{\mathbf{E}}{E} \cdot d\mathbf{P} \quad (3.40)$$

Hence  $dU_{e2}$  is given by

$$dU_{e2} = -\mathbf{E} \cdot d\mathbf{P} \quad (3.41)$$

By summing equation 3.38 and 3.41, we can get

$$dU_e = -\frac{1}{2} \mathbf{E} \cdot d\mathbf{P} \quad (3.42)$$

If we differentiate equation 3.35, we get

$$d\mathbf{P} = \varepsilon_0 \Delta \chi (\mathbf{E} \cdot d\hat{\mathbf{n}}) \hat{\mathbf{n}} + \varepsilon_0 \Delta \chi (E \cdot \hat{\mathbf{n}}) d\hat{\mathbf{n}} \quad (3.43)$$

If we substitute equation 3.43 into equation 3.42, we get

$$dU_e = \varepsilon_0 \Delta \chi (\mathbf{E} \cdot d\hat{\mathbf{n}})(\hat{\mathbf{n}} \cdot \mathbf{E}) + \varepsilon_0 \Delta \chi (E \cdot \hat{\mathbf{n}})(d\hat{\mathbf{n}} \cdot \mathbf{E}) \quad (3.44)$$

$$dU_e = -\varepsilon_0 \Delta \chi (E \cdot \hat{\mathbf{n}})(E \cdot d\hat{\mathbf{n}}) \quad (3.45)$$

However, we can parameterise  $\hat{\mathbf{n}}$  using  $\theta$ , we can then conclude that

$$\mathbf{E} \cdot \hat{\mathbf{n}} = E \sin \theta \quad (3.46)$$

$$\mathbf{E} \cdot d\hat{\mathbf{n}} = E \cos \theta d\theta \quad (3.47)$$

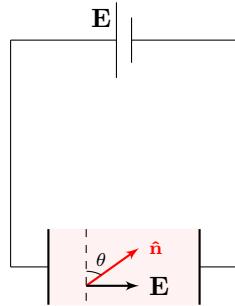


Figure 53: Caption

Then we can integrate  $dU_e$ , we get

$$\int_0^{U_e} dU_e = -\varepsilon_0 \Delta \chi E^2 \int_0^\theta \sin \theta \cos \theta d\theta \quad (3.48)$$

$$U_e = -\frac{1}{2} \varepsilon_0 \Delta \chi E^2 \sin^2 \theta = -\frac{1}{2} \varepsilon_0 \Delta \chi (\hat{\mathbf{n}} \cdot \mathbf{E})^2 \quad (3.49)$$

Using the same argument, you can get the magnetisation, which is

$$U_M = -\frac{1}{2} \mu_0 \Delta \chi_m H^2 \sin^2 \theta = -\frac{1}{2} \mu_0 \Delta \chi_m (\hat{\mathbf{n}} \cdot \mathbf{H})^2 \quad (3.50)$$

However, if we polish the surface carefully (fig 54a) or take a surfactant molecule (figure 54b), we can force the polymer to align in a specific direction.

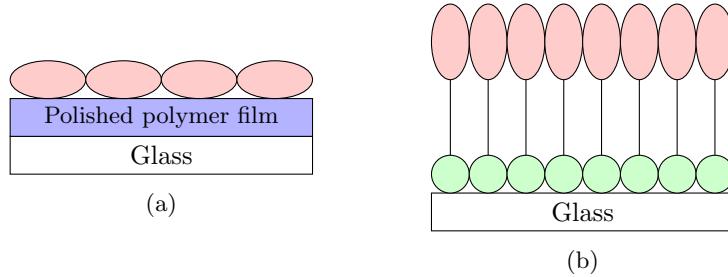


Figure 54

We will investigate the effect of electric field and the boundary condition on the polymer.

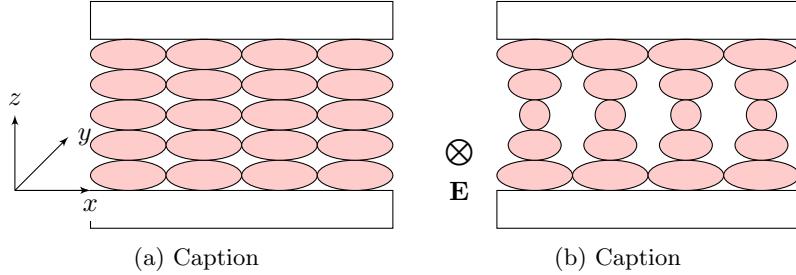


Figure 55

Before applying an electric field, the polymer was fixed, we assume wolg they are pointing in the  $x$  direction. As shown in figure 55a. If however, we apply an electric field, for example in the  $y$  direction, the bottom and top polymer is pinned, but the other polymer will rotate to the  $y$  direction. But this produce a torsional energy. The overall energy at a given  $z$  was shown in equation 3.51.

$$U(z) = \frac{1}{2}K \left( \frac{d\theta}{dz} \right)^2 - \frac{1}{2}\varepsilon_0\Delta\chi E^2 \sin^2 \theta \quad (3.51)$$

Note that  $U$  depends implicitly on  $z$ , we want to find the function  $\theta$  that minimise the functional integral

$$G_A = \int_0^d \left[ \frac{1}{2}K \left( \frac{d\theta}{dz} \right)^2 - \frac{1}{2}\varepsilon_0\Delta\chi E^2 \sin^2 \theta \right] dz \quad (3.52)$$

If we insert equation 3.52 into the Euler-Lagrange equation

$$\frac{\partial G_A}{\partial \theta} - \frac{\partial}{\partial z} \left( \frac{\partial G_A}{\partial \theta'} \right) = 0 \quad (3.53)$$

We will get

$$\frac{1}{\sin \theta \cos \theta} \frac{\partial^2 \theta}{\partial z^2} - \frac{\varepsilon_0 \Delta \chi E^2}{K} = 0 \quad (3.54)$$

People find that there is no analytical solution to equation 3.54 , so they solved this equation numerically,

It turns out that the polymer will start to twist only if electric field is *greater* than *Freedericksz potential*  $E_F$  (don't mess up with Fermi level)

$$E_f = \frac{\pi}{d} \sqrt{\frac{K}{\varepsilon_0 \Delta \chi}} \quad (3.55)$$

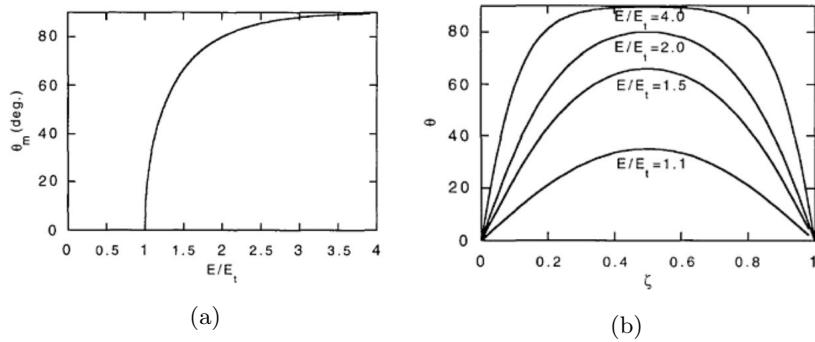


Figure 56

Note that the twisting is the easiest thing to analyse, depending on the direction of electric field and boundary condition, one can also bend or splay the molecule.

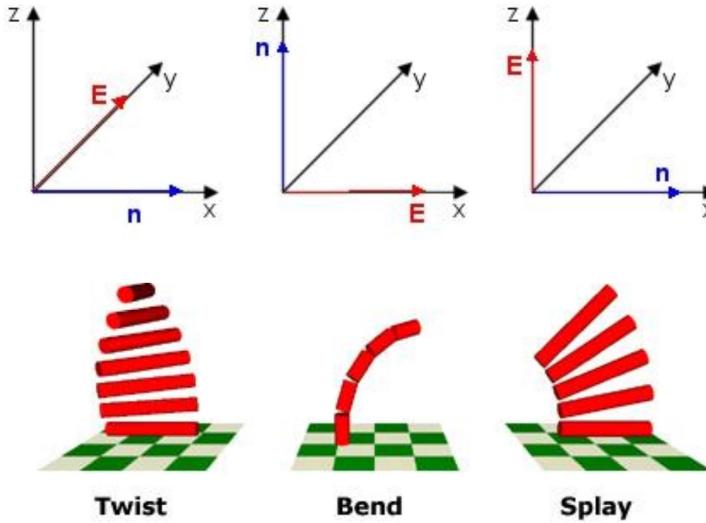


Figure 57: Caption

Now consider the chiral nematic molecule, without applying electric field, the arrangement of molecule is such that it rotates gradually over z direction

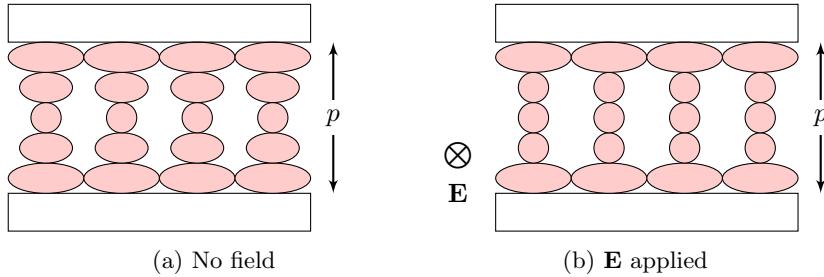


Figure 58

Consider figure 58, without applying electric field, the director will rotate gradually, as discussed in the previous subsection, 50% of unpolarised light will transmit through. However, if one applies an electric field perpendicular to the director of the top and bottom layer, which exceeds  $E_F$ , the rest of polymer will start to switch perpendicular to the top and bottom layer. This blocks all the light transmitting through. This is called helix unwinding.

### 3.4 Liquid crystal displays

The basic structure of liquid crystal display was shown in figure 59. Note that light comes from right to left, and goes back. We have two polarizers, there are two *transparent* electrodes in between (aligned parallel to the director). Between the electrodes, there is a chiral nematic liquid crystal layer.

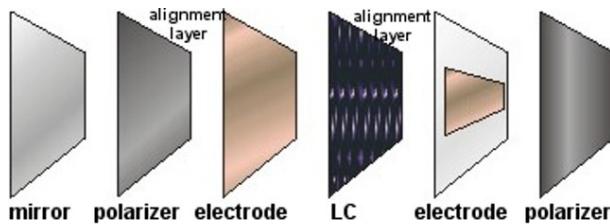


Figure 59

Now if we apply an electric field to the liquid crystal, the liquid crystal will tend to align with the field, as discussed before. Light will not be able to move with the director. Thus it will get absorbed. (Note since the electric field in two electrodes are perpendicular, the molecule will twist in a complicated shape, shown in figure 60).

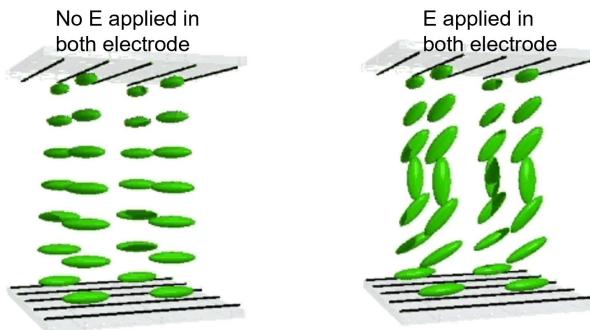


Figure 60: Caption

What people do is they put three different chiral nematic molecules into a pixel. Each subpixel can switch on and off. If it switches on, then it absorbs all light. Then people apply a color filter on the bottom, to filter the light to one of RGB.

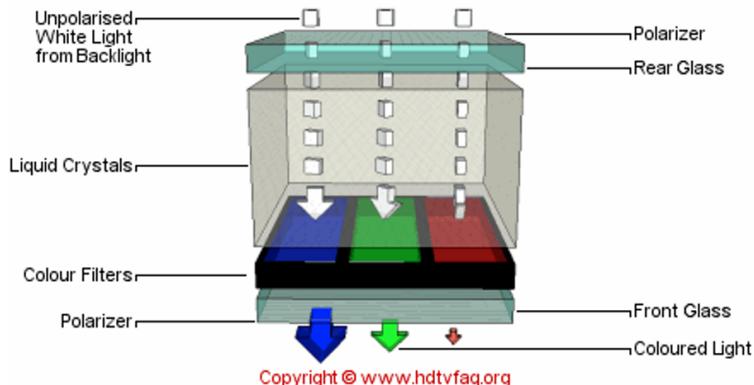


Figure 61

The *multiplexing* process is more easy for liquid crystal display. People apply a positive row signal, which correspond to 0.8 of  $E_F$ . They apply row signal *one at a time*. But it is less than  $E_F$ , so nothing will happen. People apply a negative column signal *continuously*, again correspond to 0.8 of  $E_F$ . If the liquid crystal receive the signal from both electrodes, then the potential difference exceed  $E_F$  and Freedericksz Transition take place. Now we will look at the material requirement of liquid crystal display. They have to have large difference in relative permittivity in the ordinary and extraordinary direction. I.E. high  $\Delta\epsilon$ . It has to be stable over a wide temperature range. This can be achieved by mixing different chiral nematic molecule at different fraction. It has to be transform immediately over a small voltage range. I.E. high sharpness.

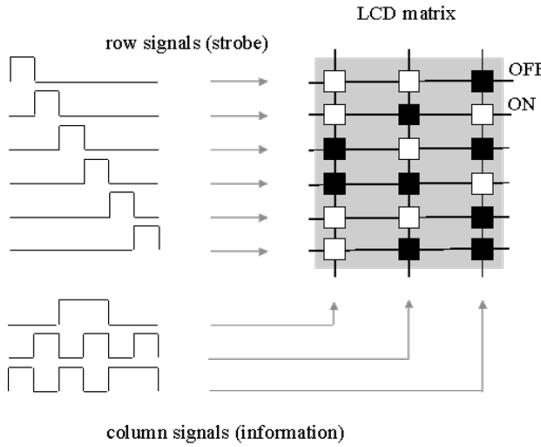
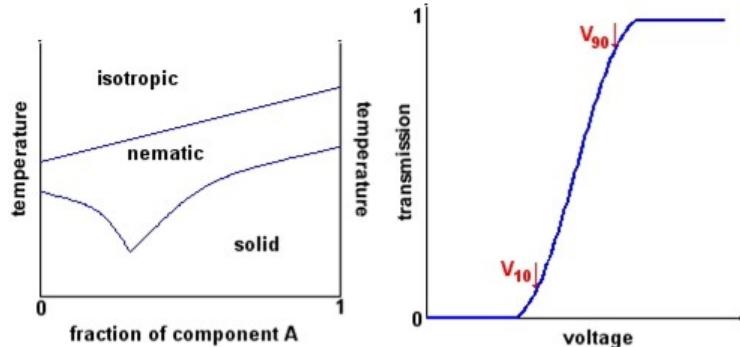


Figure 62



(a) Mixing different fractions of A give a higher temperature range of difference in the voltage to cause nematic phase.  
 (b) Sharpness was defined as the 10% and 90% transition.  $V_{10}$  and  $V_{90}$

Figure 63

Another important display device is active display, where we put a field effect transistor in each pixel. As introduced in the MSE 105 course, it need a gate voltage and a voltage between source and drain to flow the current. The challenge is we should put all these pixel and still make them work. When you put each pixel in, they are likely to block the light.

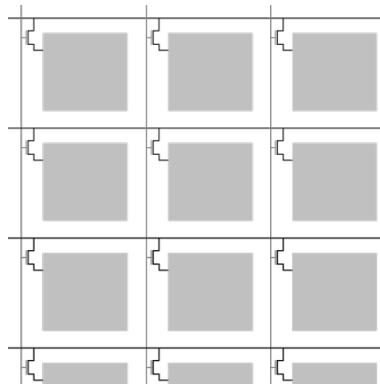


Figure 64: Caption

A typical example of active display is TFT display(lecture 8, slide 9). It was not gont into detail, but i think it is worth noting that the complicated structure allow shading to be controlled more easily. (you can have gray rather than just black and white).

Note that the liquid crystal was manufactured in small batch. It is not like steel, where million tonnes was manufactured. Tonnes of liquid crystal is sufficient to supply the while world. Now people are staring to play with organic LED. This again gives differnt pixel, and allow to switch on and off. But since it is not explainable for 3rd year, i am unlikely to do the note.

## 4 Solar cells

### 4.1 Some basic terminologies.

Solar cell one of the fuel technique that has the highest potential. The total incoming sunlight has power of 174 PW, which is much larger than the Energy consumption in 2004. (15 TW). So it is worth developing solar cells that harness these energy. To understand the solar cell technique, we shall first look at some definitions.

**Definition 4.1** (Insolation). Insolation is the power per unit area of solar energy that reaches the earth's surface

**Definition 4.2.** *Direct* means use a single transform to convert sunlight to useful energy. (Photovoltaic, thermal mass, direct water, solar cell)

**Definition 4.3.** *Indirect* means uses multiple transform to convert sunlight to useful energy(biomass, hydroelectric, wind, ocean thermal, fossil fuels.)

**Definition 4.4.** *Passive* means using non-mechanical techniques to capture solar energy(Building design)

**Definition 4.5.** *Active* means Use electrical or mechanical components to change solar energy to useful form. (Photovoltaic cell, solar towers)

We will look at some example of Passive solar cell.

**Example 4.1.1.** A typical example of *Passive solar* is basically just use sunlight to light the room, instead of e.g. light bulb. So the building designer should design the window carefully to get as much light in as possible.

However at hot summer, if we prevent the sunlight from coming, then we do not need cooling. This can be achieved by careful design of building.

**Example 4.1.2.** For *Trombe walls*, it is designed as follows, the summer light tend to incident at a steeper angle compared to winter light, thus a block was applied on top of building, which block summer sunlight, and allow winter sunlight to come, Apart from that, the window is designed such that it allows light in, but don't let them travel out. In addition, to prevent the situation when it is too hot at noon, and too cold at night, a metal wax was put behind the window, at daytime, the temperature is so hot that these wax melts, which absorb heat, in the evening, as the wall cools, the wax solidify, which release latent heat, and the room become warm again.

Now we will look at some example of *active solar*

**Example 4.1.3.** For a *Solar tower*, it is surrounded by a lot of mirror, these mirror reflect all the light to the tower, these light energy was then used to heat salt water, these heat salt was then passed through a steam generator to convert energy.

**Example 4.1.4.** For a *Solar pond*, it has a pond with a salt gradient. As sunlight pass in the pond, it is unlikely to be absorbed by water, it is most likely to be absorbed near the bottom, the salt gradient avoid heat convection. These water in the bottom was then taken and used to convert energy.

After looking at numerous examples, we will now consider the economics of solar cell.

**Definition 4.6.** The *economics in terms of pay back time*  $E_{PBT}$  is defined as

$$E_{PBT} = \frac{E_{\text{man}} + E_{\text{trans}} + E_{\text{inst}} + E_{\text{use}} + E_{\text{decom}}}{E_{\text{gen per annum}}}$$

Where we have taken account all the energy consumed during the lifetime of the solar cell. Including its decomposition, and see how long needed for the solar cell to generate enough energy to overweight the energy consumed during its lifetime.

But  $E_{PBT}$  alone is not sufficient, if a solar cell has very short  $E_{PBT}$ , but its lifetime is even shorter, then we are wasting energy. So instead, we consider another parameter to evaluate the solar cell.

**Definition 4.7.**  $EYR$  is defined as

$$EYR = \frac{E_{\text{gen}} L_{PV}}{E_{\text{input}}}$$

It measures *how many times* the energy input i can get throughout the lifetime of the solar cell.

Note that the household has two options, either to use the energy by their own(*Stand alone*) or they can sell it to the government. (*On grid*). The latter is has a shorter Energy payback time and a higher  $EYR$ .

## 4.2 Principle of solar cells

In figure 65, it shows that the charge carriers separate as light was incidented, After around femtoseconds  $10^{-15}s$ , the carriers relaxed to the top of VB and bottom of CB, but after microseconds, the charge carrier will recombine, this is a process that we want to avoid. In figure 65, it used some sort of electric field to separate the charge, so the electron goes RHS, while holes goes RHS. In order for solar cells to work, we need to introduce some *Asymmetry* into our system. This can be done by using a *Schottky Junction* (junction between a metal and semiconductor), or a p-n junction. Which has a bias, causing opposite charge carriers to go in opposite directions.

It should be noticed that the circuit in a solar cell is equivalent to the circuit shown in figure 66 (in the non-ideal case, in ideal case,  $R_S = R_{SH} = 0$ ), This is called an equivalent circuit . Now we will introduce some definitions.

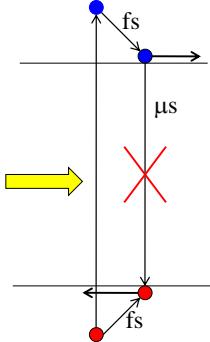


Figure 65: Process take place in solar cell

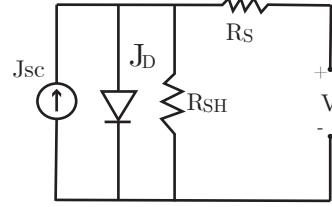


Figure 66: equivlent circuit

**Definition 4.8.** As shown in figure 66, the *Current!Short circuit current density*<sup>1</sup> is the current *drawn* when the terminals of solar cells are connected. ( $V = 0$ ) [1]

$J_{sc}$  can also be calculated in equation 4.1. Where  $QE(E)$  is the probability that a photon with energy  $E$  will deliver one electron to an external circuit.  $b_s(E)$  is the incident *photon flux density* with energy  $E$ . It should also be note that in some case, people uses  $\lambda$  instead of  $E$ , and they are related by  $E = \frac{hc}{\lambda}$ .

$$J_{SC} = e \int b_s(E) QE(E) dE \quad (4.1)$$

**Definition 4.9.** Dark current density  $J_D$  is the current generated by this equivalent current an applied *bias*  $V$ , *in the dark*. It can be calculated using equation 4.2

$$J_d = J_0 \left[ \exp\left(\frac{eV}{kT}\right) - 1 \right] \quad (4.2)$$

The total current is the sum of the dark current and the photocurrent (they are in opposite directions), as shown in equation 4.4

$$J = J_d + J_{SC} \quad (4.3)$$

$$J = J_{SC} - J_0 \left[ \exp\left(\frac{eV}{kT}\right) - 1 \right] \quad (4.4)$$

**Definition 4.10.** *Open circuit voltage* is the voltage which there is no *current* produced.

Open circuit voltage can be calculated by equation 4.5

$$V_{OC} = \frac{kT}{e} \ln \left( \frac{J_{SC}}{J_0} + 1 \right) \quad (4.5)$$

---

<sup>1</sup>Note that  $I$  implies current,  $J$  implies current density, they are related by  $I = JA$

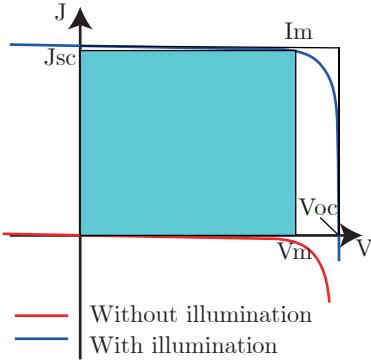


Figure 67: J-V curve for a solar cell

**Definition 4.11.** The fill factor is the ratio between the cyan triangle and the outer triangle, shown in equation 67, it can also be calculated using equation 4.6

**Definition 4.12.** The area of rectangle in side the blue curve of figure 67 correspond to the output power of the solar cell, The cyan rectangle is the biggest possible that can be drawn. The  $J$  and  $V$  correspond to this maximum power output is  $J_M$  and  $V_M$ .

$$FF = \frac{V_M J_M}{J_{SC} V_{OC}} \quad (4.6)$$

Using all these equations and definitions, the power output is given by

$$P = FF \times J_{SC} \times V_{OC} \quad (4.7)$$

There are other two important factors that reduced the Fill factor significantly, according to figure 66, in fact the equivalence circuit has two resistor connected to it, one in series (*Series resistance*) and one in parallel to the current (*Shunt resistance*). They can reduce the fill factor of the cell in the manner shown in figure 68 and 69.

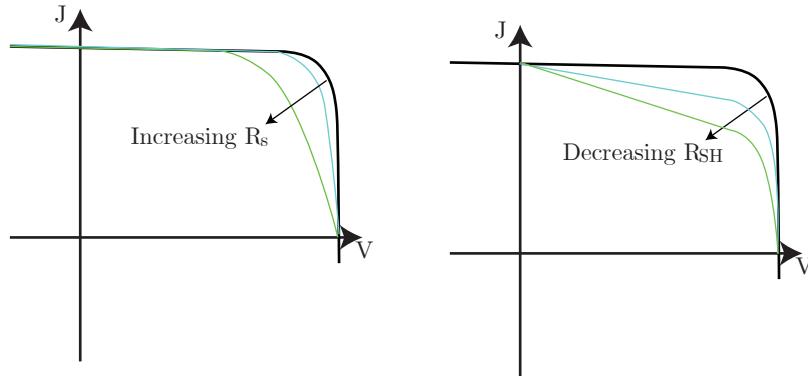


Figure 68: Effect of  $R_s$  on the solar cell

Figure 69: equivalent circuit

**Definition 4.13.** IPCE stands for Incident photon-to-current efficiency (or quantum efficiency), it is a measure of how efficiently the device converts the incident light into electrical energy *at a given wavelength*.

Even though it is wavelength specific, this value is greater than 50% for most of the wavelength. This is because it is just the ratio of electron generated to the incident photon. Shown in equation 4.8. However, the efficiency  $\eta$  is ratio of input power  $P_{in}$  to the output electrical power  $P_{out}$ . As electrons was converted, some of energy (or V) was lost (eg. during the relaxation process). Thus  $\eta$  is lot less than IPCE.

$$IPCE = \frac{j_{ph} \times h\nu}{I} \quad (4.8)$$

$$\eta = \frac{P_{out}}{P_{in}} \quad (4.9)$$

### 4.3 Solar cell requirements

The requirement of solar cells are enumerated below. 1 should be met because all if band gap is too high, only a very small fraction of photon can be absorbed (Note that photons will be absorbed only if the energy is larger than the band gap, infact optimum value for band gap is 1.2-1.3eV). 2 should be met because for an indirect band gap material, it not only requires photon-phonon-electron coupling to excite an electron, this is unlikely to happen, it thus require a longer distance to absorb all the incoming photon.

1. Have a band gap between 1.1-1.7 eV
2. Have a direct band gap structure

3. Being cheap and non toxic
4. Suitable for large scale manufacture
5. Lossless transport
6. Possess a good PV conversion efficiency
7. Be stable in the long term (20 years).

#### **4.3.1 Silicon as a solar cell**

Silicon has a band gap of 1.1 eV, it has met all of the condition enumerated, except for condition 2. The Si-Solar cell should thus become very thick to absorb all the incoming photons. Although silicon is very abundant, it does make the solar cell very heavy, it thus cannot be used for solar cell in the universe, because the cost of sending it into the space is too high. Nevertheless, 83% of solar cells in 2010 was produced by silicon, because of all other merit of silicon. How can we avoid the consequence of not being a direct band gap solar cell?

Figure 70 shows a typical band diagram for a schottky junction. There are three important regions in it, the  $d_{sc}$  region, the  $L + d_{sc}$  region, and the  $\frac{1}{\alpha}$  region. In the space charge region, where  $x < d_{sc}$ , the VB and CB bands, it should be noted that electrons tend to go downwards in energy(so it will go to LHS), and holes tend to go upwards(so it will go to RHS).  $L$  is the bulk diffusion length of the minority charge carrier(hole, It is the minority charge carrier that participate the conduction process, because i guess minority carrier go across the junction, and it is the same charge as the majority charge carrier, which means it is unlikely to get recombined, so it will conduct).

In  $x < D_{sc} + L$  region, holes are still able to diffuse back to the space charge region, in this case it can then travel across the junction. Beyond this region, holes are highly likely to get recombined. Finally,  $\frac{1}{\alpha}$  is the region where the light intensity drop to  $\frac{1}{e}$ , so we can say that most of the light get absorbed.

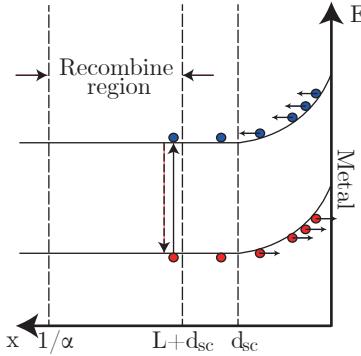


Figure 70: Schematic illustration of a schottky barrier solar cell

Now we are going to look at some silicon p-n junction, consider figure 71 and 72, i will now explain why it is designed in such a manner. The reason why one side is so thin is because we want the light to go to the *junction*, far from the junction, all the photocurrent will get recombined. The reason why we choose p side to be larger is because in the p-side, electron is the minority charge carrier, it is the minority charge carrier that precipitate the conduction process we want the minority charge carrier to travel as fast as possible, so i think this will increase the L value. Electron has lower effective mass compared to holes, it will thus travel faster.

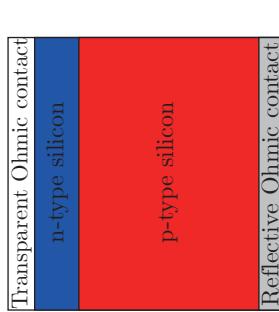


Figure 71: Schematically illustration of a Si p-n junction solar cell

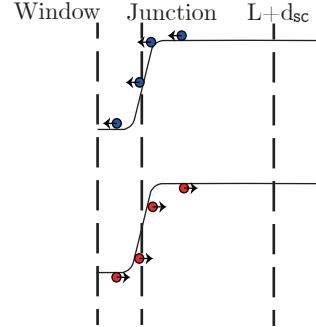


Figure 72: The band diagram of the p-n junction shown in figure 71

#### 4.4 Thin film solar cell

In the previous section we have looked at how silicon was used to produce solar cell, however, the cost of building single crystal Silicon is very high, thus silicon

solar cell might not be the best solar cell in terms of *cost-performance*. In this section, the thin film solar cell was introduced. Like its name, it is thin film, and we can use polycrystalline material (which has a grain size of 10 nm-1cm, and have lots of impurities) rather than single crystal, which are easier to fabricate. Although the production efficiency reduced to 13-15%, the cost reduced significantly, there are too much area that was not covered by solar cell in the earth, so overall we can harness more energy using these cells.

#### 4.4.1 Surface texturing

#### 4.4.2 Material requirements

The thin film solar cell need to have the following properties.

1. Low cost
2. Non-toxic
3. Robust
4. Stable
5. High absorbtion

Property 5 is very important because it *Relax the requirement of minority charge carrier diffusion length L*, thus polycrystalline material or amorphous material can be used(As discussed in part 4.3.1, the reason why we maximise  $L$  is because it allow electrons/holes that wasn't generated in the space charge layer to diffuse back without recombination, but if  $\alpha$  is high, then all the photo-electron and holes was generated near the junction, there is no need to maximise  $L$ ). For photons with energy greater than 1.7eV, amorphous Si absorb it better than Si, and for even higher Energy photons, it was absorbed 10 times better in amorphous silicon. This is why amorphous Si cells can be utilised.

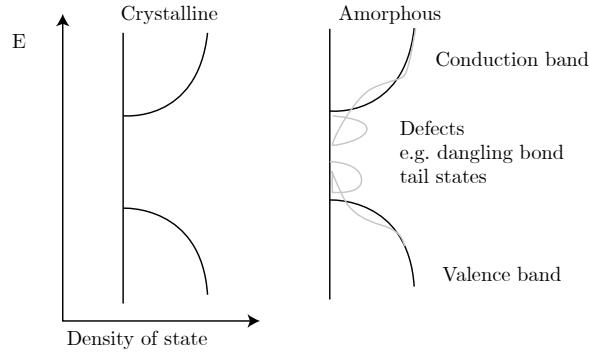


Figure 73: Band structure of amorphous Silicon[1]

The band structure of crystalline and amorphous Si was shown in figure 73, it shows that amorphous Si has a lot of *dangling bonds* in the band gap, it arises because of dangling bond defects and tail states. e.g. in the perfect Si substrate, all Si forms a continuous network, while for amorphous Si, there are a lot of, like trivalent Si, which has an unpaired electron. This helps light absorption, because in amorphous silicon, we will not get a well defined  $E-k$  relation, so there is no need for the extra phonon. At visible wavelength, the absorption coefficient is of order of magnitude greater for amorphous silicon.

However, thin film solar cell cannot operate without *Surface passivation*. The extra donors and acceptors introduced by the impurity will be captured by the dangling bonds. Surface passivation uses atomic hydrogen, they can form a bond with the unpaired electron in the dangling bond, so it is unable to capture the e/h any more. But even if the material is passivated, the doping efficiency is still low. Apart from that, the dangling bonds cause the fermi level to be pulled towards its energy level. So the fermi-level, instead of lying in the dopant level, it will lie *between* the dopant and defect level.<sup>2</sup>. It implies low junction bias. Last but not least, doping and defect will reduce the minority carrier lifetime.

#### 4.4.3 Charge transport in a-Si

The conductivity of a-Si is frequency dependent, as illustrated in figure 74(a). The reason behind that is: during the conduction process, electron is *hopping between dangling bonds*. For high AC field, electron will hop back and forth as shown in the black arrow. But for low frequency AC field, electron will hop, *followed by relaxation*. Thus more energy will be required to move the electron to the 'top of hill'. Thus the resistance is higher for low  $f$ , and it means lower conductivity.

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<sup>2</sup>The figure of [1] page 219 gives a good illustration of this.

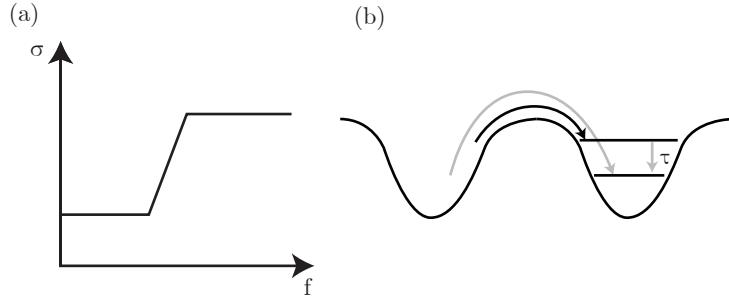


Figure 74: (a) frequency dependent of conductivity. (b) the hopping of electron in a-Si for low and high frequency.

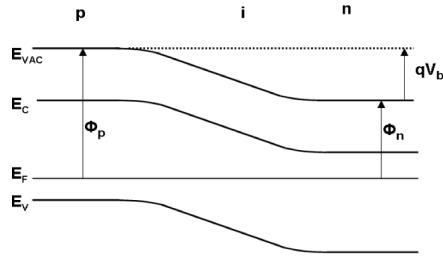


Figure 75: Schematic of a p-i-n junction

#### 4.4.4 p-i-n junctions and Hetero junction

In amorphous Silicon, the diffusion length  $L$  is very small, it is negligible compared with the space charge layer. Which means that only space charge layer contribute to light absorption. This will result in a bad efficiency. To avoid this problem, by using a p-i-n junction.

**Definition 4.14.** A p-i-n junction is a junction in which an *intrinsic layer* is sandwiched between a p-layer and n-layer. A typical p-i=n junction was illustrated schematically in figure 75

By putting an intrinsic layer between, there is a longer junction, as illustrated in 75, the whole intrinsic layer has a bended CB and VB, it encourages charge carriers to move in the direction we want (e will move downward, h will move upward). This increase the light absorbtion. To make a amorphous solar cell, one simply spray SiH<sub>4</sub> onto the surface of device, followed by heating, it will remove the H and you are left with a layer of amorphous Si. I will latex the heterojunction after i finish MO's heterojunction. But now let's just look at some other thin film solar cell.

**Example 4.4.1** (CIGS solar cell). A CIGS solar cell stands for  $Cu(In, Ga)(S, Se_2)$ . It corresponds to a very small circle of  $\alpha$  phase within the Cu-In-Se system. There are numerous benefits of using this compound. It has one of the highest absorption coefficients amongst all optical materials, which is good for thin film, and this allows polycrystalline CIGS solar cell to work. Apart from that, it has a moderate band gap of around 1 eV. More importantly, if you got a, say  $V_{Cu}$ , it will complex with the  $I_{In}$  and the energy level of this complex is *not* between VB and CB, which means it will not deteriorate the efficiency. There are two ways of forming a CIGS, the first one is to coevaporate Cu, In, Se, but this method is more expensive so it was done in the laboratory. The other method is to sputter Cu and In, followed by *Selenisation*, i.e. react in a  $H_2Se$  atmosphere (*But it is toxic*). The actual solar cell was shown in figure 76. Where ZnO is the hole collector, the CdS layer (2nm) between ZnO and CIGS acts as a buffer layer, it was deposited by *Chemical bath*, it smooths the lattice mismatch between CIGS and ZnO, which might result in carrier recombination, it also blocks the hole transfer. Mo is a contact. Nowadays, the *efficiency* achieved in lab is around 18% for co-evaporation method, and 16% for selenisation method.

**Example 4.4.2** (CdTe solar cell). There is a competitor to the CIGS solar cell—CdTe solar cell. It is easier to make compared with other thin film solar cells. To manufacture CdTe solar cells, as shown in figure 78, CdTe were put into an evaporating dish, it was then heated, then one moves the sample above the top and then the CdTe will deposit directly onto the surface. By close space sublimation, they sublimate rather than melt, which is good to make single crystals. The preferred design for CdTe is n-CdS p-CdTe, as shown in figure 77. However, Cd is toxic, which is not a desirable property of solar cells.

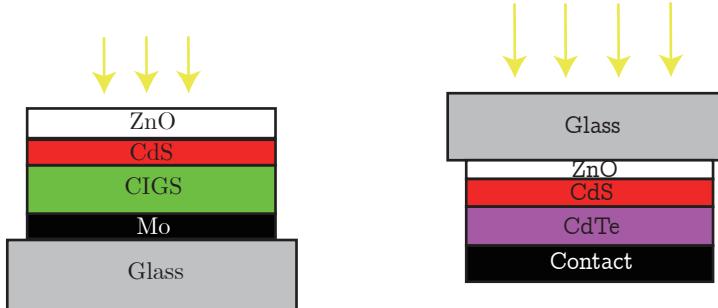


Figure 76: Schematic of CIGS solar cell

Figure 77: Schematic of a CdTe solar cell.

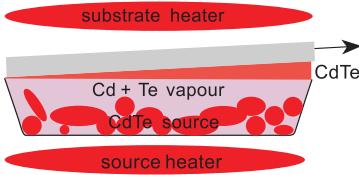


Figure 78: The deposition method of CdTe onto solar cell

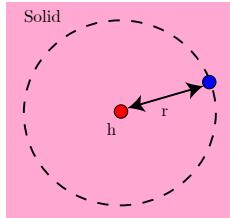


Figure 79: Schematic of an exciton

## 4.5 Excitonic solar cell

Now we will introduce one of the best solar cell interms of cost and efficiency- Excitonic solar cell, we will now explore what makes it such a good solar cell. But first, we need to introduce what an *exciton* is.

**Definition 4.15.** An *exciton* is a pair of hole and electron *bond together*, with the electron *orbiting* the hole. A typical exciton was shown in figure 79.

For a *Mott-Wannier* exciton, the radius of exciton is *larger* than the lattice spacing. The binding energy of this exciton is around 0.1eV, they are weakly bonded. Whereas for the organic phase material, the dielectric constant, the exciton inside is usually *Frankel* exciton. The radius of this exciton is approximately the same as the lattice constant. The e/h pair are strongly bonded, the bonding energy is around 1 eV.

### 4.5.1 Excitonic solar cell

To build a solar cell, a layer of porphyrin, structure shown in figure 80 was sandwiched between two ITO layer. As illustrated in figure 81. As mentioned earlier, to harness the sunlight, we need some asymmetry in the sunlight, as we will show below, for the solar cell introduced in figure 81, the asymmetry come from the sunlight.

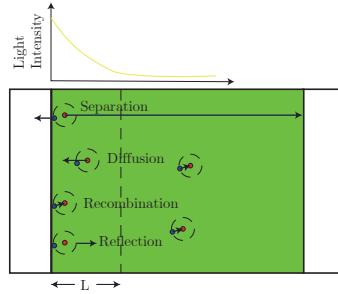


Figure 82: Schematic of Separation, diffusion recombination and reflection process taken place in Excitonic solar cell.

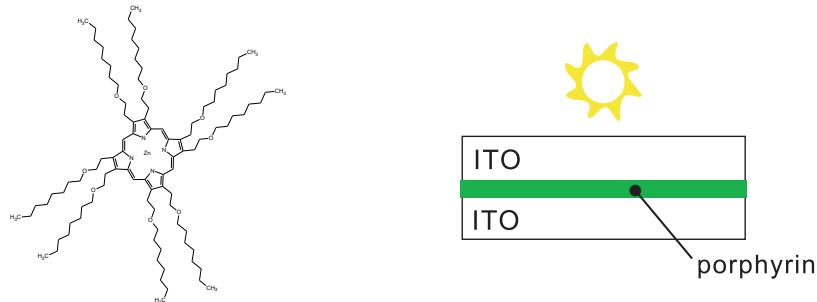


Figure 80: Schematic of the chemical structure of porphyrin.

Figure 81: Schematic of an excitonic solar cell.

Now we will discuss the process taken place within the excitonic solar cell. Consider figure 82, when the exciton touches the junction, charge separation might take place, the electron goes into the anode(the anode only accepts the electron, not the hole.), and since porphyrin is a good hole conductor, the hole will move right accross to the other electrode. However, the holes need to *diffuse* to the ITO,  $L$  is the diffusion length of exciton, it is around 20 nm, beyond this length, the exciton is likely to recombine. So to improve the performance of solar cell, one needs to increase  $L$ , or allow all light to be absorbed within  $L$ . However, there are two other process that might also take place with in the surface, *reflection* and *recombination*. i.e. the exciton might bounce off the surface. Or if one do not design the surface properly, it might enhance recombination, i.e. the surface take the electron *and* give it back to the hole. So we need to *Increase separation, decrease reflection and recombination*.

To improve the efficiency further, we will introduce an asymmetry within the cell, rather than relying on the light to create the asymmetry. The way to do that is to combine a donor layer together with an accepter layer. Probably both of the layer can absorb light, one can absorb low wavelength light, other will absorb high wavelength light. Apart from that, the charge pair will go to

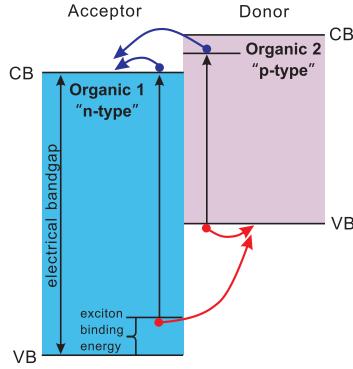


Figure 83: Caption

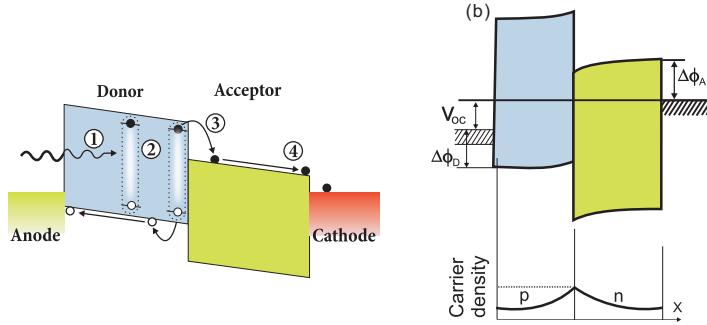


Figure 84: Caption

donor/acceptor cite, as shown in figure 83.

Another way of avoiding recombination is to move the electron from a singlet state to a charge transfer triplet state. As you move through the triplet state, the spin of the charge will get fliped, thus it will not recombine with the holes.

Apart from avoiding charge recombination, we also need to enhance charge collection in the electrodes. What we do is we put a small energy difference between the VB/CB edge and the metal work function. This difference is termed  $\Delta\phi_D$  and  $\Delta\phi_A$  respectively. As illustrated in figure 84.

But this method will deteriorate  $V_{OC}$  significantly. Some people might doubt why don't we just use a work function that is very very close to the CB/VB? it turns out that there is no effect on the open circuit voltage. In figure 85, it shows that e/h are accumulated in the junction between the electrode and the organic layers. Which also deteriorate the  $V_{OC}$ .

It turns out that the problem we about  $V_{OC}$  deterioration can be solved by a improved design. In this design, instead of two distinct 'n' and 'p' layer, we used *mixture* of layer. As illustrated in figure 86. We can see 'sea' of one

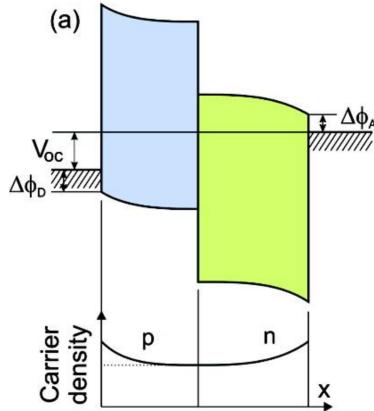


Figure 85: Caption

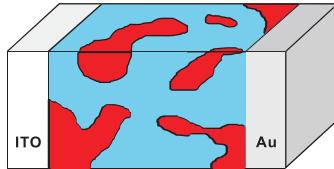


Figure 86: Caption

organic material, e.g. the 'n-type' organic layer. In which there are 'island' of another mateial. Note that the 'sea' material has procolated. i.e. the electrons can travel all the way from one site of electrode to the other site. The size of 'sea' and 'island' are approximately 20nm, this is typically the diffusion length of the exciton. Interestingly, if the light was not absorbed between one interface between two materials, it might absorb in another interface nearby. This guarentee that all the light was absorbed to do the right thing.

As promised, the  $V_{OC}$  is now dependent on the work function. You now have to make the work function close to the CB/VB. The effect of work function on the  $V_{OC}$  was illustrated in figure 87.

I will L<sup>A</sup>T<sub>E</sub>Xthe inverted cell bit later.

#### 4.5.2 Dye sensitized solar cell

Now after discussing a lot of solar cell, we will introduce the best best solar cell in terms of cost-economy and whatsoever. This is the *dye-sensitized solar cell*. A typical dye sensitized/Gratzel solar cell was illustrated in figure 88. It has a TiO<sub>2</sub>+dye layer sandwitched between two transparent conductive oxide

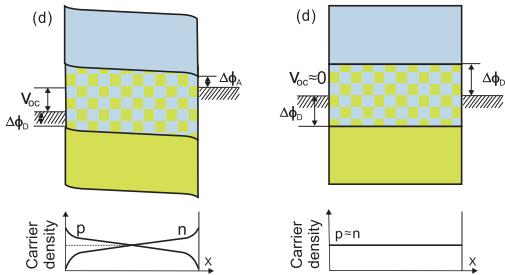


Figure 87: Caption

(TCO) layer. The TiO<sub>2</sub> was made to be very *porous*, it was coated with a layer of dye. And we put  $I^-$  and  $I_3^-$  into these pores, which is like an electrolytes. The reason why we use liquid instead of solid is because the TiO<sub>2</sub> is too porous, it is impossible to form electrical contact between the two.

After discussing the basic structure, i will discuss how the system generate light. Firstly, the light was absorbed in the interface between the dye and the TiO<sub>2</sub>, the electron get transferred through the TiO<sub>2</sub>, while the dye was left oxidized. Secondly, the  $I^-$  flow to the oxidised dye, and reduce the dye. The  $I^-$  get oxidised to  $I^{3-}$ . Meanwhile, as the electron flow through the TiO<sub>2</sub> and reach the cathode, it will conduct through the external circuit, and *do work*, then go to the cathode. The  $I^{3-}$  will flow to the cathode, pick up the electron, and reduce back to  $I^-$ . So overall nothing inside the solar cell has changed, except that solar energy is converted. The whole process was illustrated in figure 89.

When Gratzel proposed this solar cell, the efficiency is 10%. People believe that they can improve the efficiency shortly, but in fact they spent a few years before finding an idea to improve it. The problem is that there are several factor that causes energy loss, shown in figure 90, if they improve one factor, it deteriorate the other factors. We will discuss some factors in this note.

The first problem is that the dye are too thin, there are only a few states within. As light shines, all the electrons goes to the CB, we know from MSE 105 that fermi-level is defined as the energy level where the probability that an electron was occupied is 0.5, In this case as light was shine onto the dye, there are a lot of electrons near CB. The fermi level is close to the CB. In fact this is not a fermi-level, it is a *pseudo fermi level*. The voltage we can get from this system is directly related to the difference between the  $E_F$  in the TiO<sub>2</sub>and the liquid.

**Definition 4.16.** A *pseudo fermi level* is the level where the probability of finding an electron is 0.5, but *not under equilibrium*.

Another thing we can improve is the dye, the improved dye was illustrated schematically in figure ??, But originally, the structure was like ???. Some people are improving the efficiency of this solar cell by making the dye even more complicated.

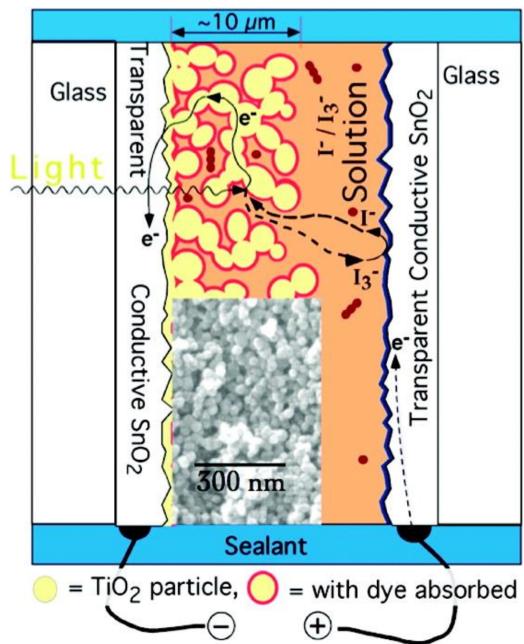


Figure 88: Schematic of a Gratzel solar cell.

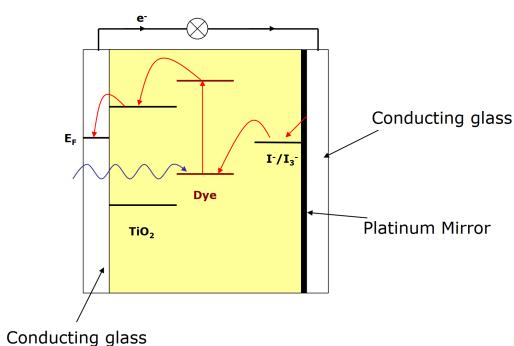


Figure 89: Energy diagram and process taken place in Gratzel solar cell.

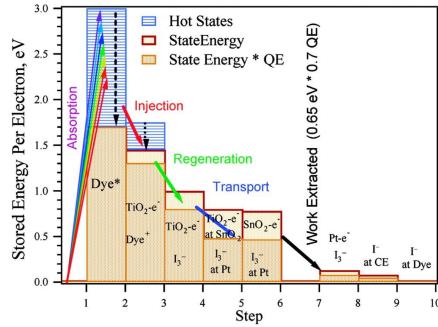


Figure 90: Factors that causes energy loss in dye sensitized solar cell.

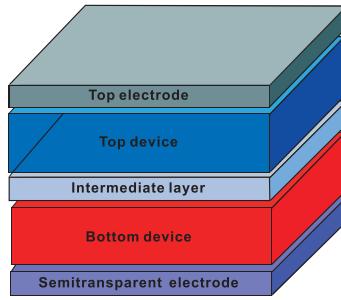


Figure 91: Caption

Can we find a material that perform better than TiO<sub>2</sub>? It turns out that ZnO worded, but the efficiency decreased. For other materials, they don't even work. This is because electron can transfer within the porous material, but it can also transfer back into the solution and recombine. But this problem do not occure in TiO<sub>2</sub>. Gratzel has also chosen the right material to regenerate the gye, i.e.  $I^-$ . Now all we need to worry about is some thing like diffusion.

I will  $\text{\LaTeX}$  the charhge transport later.

#### 4.6 Tandem soalr cell

We will finally introduce the best solar cell in terms of efficiency-Tandem cells, as illustrated in figure 91. The idea is to join different devices, they are good at absorbing different wavelength of light spectroscopy. The principle of work is as follows.

## References

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