

國立交通大學

物理研究所

碩士論文

共軛高分子熱電洞電晶體

Conjugated Polymer Hot Hole Transistor



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摘要

近年來有機半導體/傳導材料不只是重要的一們研究課題外，更有商品化的產品進入日常生活之中,例如小型有機顯示器。由於基本特性的不同越來越多的有機光電元件逐漸被研究及發展,例如記憶體,電晶體極發光二極體，產生了所謂的有機電子學(Organic Electronics)。基本的操作元件原理還是建立無機半導體元件的基礎上，也如同無機半導體一樣目前有機電晶體最多人研究的結構還是場效電晶體的結構，由於有機半導體載子遷移率較低，因此有機場效電晶體的結構有其根本上的限制,例如操作速度慢及輸出電流小,若要達到與無機電晶體相同的表現則須增高大量的製造成本.因此我們希望製造出低成本，製程容易且可到達應用要求的電晶體,而我們根據我們的需求,找到在無機半導體元件中所謂的金屬基極結構,目前並沒有此一結構的有機電晶體,而我們製作出來第一個有機熱電洞金屬基極電晶體,有很好的操作表現,電流增益可達到 29,輸出最大電流在 5 伏特時即可到達 25 毫安培.可說是已達到初期的目標，未來以應用元件水準為目標持須再進行研究

關鍵字: 有機電子學 有機場效電晶體 有機熱電洞金屬基極電晶體

Abstract

Recently organic semiconductor/conductor is not only an important but also there are more and more commercial products, for example: small organic display. Due to the basic characteristics differences of organic device, there are more and more organic device in the research and develop, for examples: organic memory, organic transistor and LEDs, and this is what we call the “organic electronics”. Most organic devices operation principles are base on the inorganic semiconductor device theory. For organic transistor, as the same as the inorganic electronics, most devices structure were the structure of field emitting transistor. Because the organic material low mobility, there are some intrinsic problems of organic transistor. For example, low operation speed and small output current. If the organic transistors want have the same performance as inorganic transistors will increase lots of cost. So that, we hope to made a low cost, easy process and the performance will achieve the level of the require of commercial product. According to our requirement, we found the metal base structure in the inorganic electronics. And there is no this types all organic transistors in the world. The organic metal base transistor what we made have nice performance, which the current gain up to 29, maximum output current 25uA at the operation voltage just 5 volts. Future work’s goal is the transistors operation performance good enough be the commercial product.

Keyword: Organic electronics, Organic field emit transistor,
Organic hot hole metal base transistor

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Chapter 1: Introduction

1.1 Abstract

Organic semi-conducting / conducting material not only is a research topic but also can be some commercial products such as OLED displays and Organic FETs. Due to different characteristics of organic devices comparing with inorganic material devices, more organic devices are studied and invented. These organic devices are made in the organic or partial organic materials. These devices were called the organic electronics [1]. In this chapter, we introduce the advantages of organic electronics devices, the problems of the FET structure, the motivation of developing Polymer Hot Hole transistor and comparing with the inorganic electronics at the last..

1.2 The Characteristics of Organic Electronics

In the field of organic electronics, the devices include the luminance and electronic devices. In this section, what we called organic electronics include both kinds of devices. Comparing to materials characteristics of inorganic electronics , the characteristics of organic electronics are low cost, easy processed and flexible.

The cost of organic electronic device is much less than inorganic device because the materials and the making processes between these two kinds of devices. First, about the materials, for the inorganic electronics, are to make a stick of single crystal of Silicon. Making single crystal needs to control actuate carefully, and the yield limit by the equipment size. However, in the organic electronics, the materials are made in the way of chemical synthesis. Chemical synthesis processes can be transfer to chemical industry processes which will not limit by the equipment size and have high yield. Second, the inorganic electronics need extremely complicated processes includes CVD, implant, furnace and several different processing. Those equipments are very expansive comparing to the inorganic electronics processes equipments.

The processes of organic devices are much easier than the processes of inorganic devices. The inorganic devices' processes are so complicated that need a textbook to introduce all the details. The processes of organic devices are so easy that we can introduce as followings. There are three major ways to deposit organic materials on the structure. The three ways are evaporation, inkjet printing and spin coating. First, materials are deposited by thermal evaporation. Thermal evaporation is the main way to deposit small molecular organic materials, the advantages are that the parameters could be control easily and multi layers devices are easily made. But the disadvantages are need in the high vacuum chambers. The second way to deposit the organic material is inkjet printing which is similar to the inkjet printer operation. All we need is just to put the material in the solution then jet through the inkjet head. For large area substrate, the advantages are easy to define the pattern and equipments in very low costs. In the opposite, the disadvantage of inject printing is the difficulty to control the small size pattern like transistor channel defining. The third way is spin coating which is the same as the photo resistance deposit on the wafer. The thickness is controlled by the spin speed and the solution properties. The advantage is that it is easy to control the film thickness. The disadvantage of making multi-layer structure is that solvent melts the layer under the layer what we deposit first. As the result, it is difficult to make multi layers devices. Although we do not list all the ways of depositing materials, the ways of depositing organic material are much easier than the inorganic devices processes. We do not need to have many processes to change the material properties through the mechanical ways because the properties could be changed in the ways of chemical synthesis,

Finally, the organic electronic device can be flexible. For developing the organic electronic, flexibility is the most attractive point, because inorganic device structure is limited by the Si crystal structure. Moreover, the structure of the organic materials is

non-crystal. Many argue whether the flexible device can be functioned when it is bended. Regarding this issue, it was proved that organic device can work when it bending.

In conclusion, the characteristics of organic electronics are low cost, easy processing and flexible. Regarding these characteristics, there are many applications in the future included memory [2], RFID, flexible monitor, portable cell phone and etc.

1.3 The Problems of Organic FET

The same with the field of inorganic transistors, the most popular structure of organic transistor is field emitting transistor structure (FET). This structure has some intrinsic problems of the devices that made in organic materials because the mobility of organic materials is much lower than the mobility of inorganic materials. The problems of organic FET are low output current, high operation voltage, high cost and the low operation speed.

The output current of FETs are decided by the equation:

$$I_D = \frac{WC_i}{2L} \mu (V_G - V_T)^2 \quad (1-1)$$

Where I_D is the drain current that equal to the output current, W is the channel width, L is the channel length, C_i the capacitor of the oxide, μ is the carrier mobility, V_G is the gate voltage and V_T is the threshold voltage.

Due to the low carrier mobility of organic materials, the output current is too low. For example, the highest mobility of polymers is P3HT, the mobility of P3HT about 0.2V/cm and the Si about 100 V/cm. In the same structure parameters, the organic FET output current much less than the inorganic FET in Si. The current order is proportional to the mobility ratio.

If we hope the organic FET has the same operation performance as the inorganic

FET, there is another way that is organic FET operated in higher voltage. As now, the general maximum operation voltage of organic FETs is about 40 volts or higher to 100volts. This operation voltage order is not useful as the product that used in the daily life. So there must be having another way to increase the output current.

The last way is to reduce the channel length. If organic FETs have the same current output with the inorganic FET, the channel must reduce to sub-micron meter. The problem is to lithography because the equipments will spend lots of the cost to achieve this goal.

Final, the operation speed of FET will limit by carrier mobility. The transport speed is relative slow. And there is an intrinsic capacitor in the FET structure, the operation will limit by the capacitor relaxation time.

In a word, the problems of organic FET are low output current, high operation voltage, high cost and low operation speed.

1.4 Organic Vertical Channel FET

There is another chance of polymer FET to solve some problems. That is let the film thickness of FET the same with the channel length of FET. The ways of organic materials' deposit most are easy to control the film thickness that does not need high cost. However the processes do not need small channel length lithography. The processes of making organic vertical channel FET need some special ways to make the channel of organic FET. For example, micro meter mechanical emboss to shape the vertical channel of V-grove FET (figure 1-1). The structure is the same with the VMOS FET in the inorganic electronics [3]. The disadvantages are not suit for integrated circuit, the technical skill to make the equipment. The most important problem is the problems of organic FET do not solve because the basic operation principle is the same.

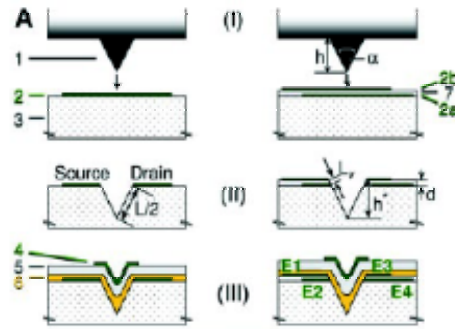


Figure 1-1 Embossing to make a VMOS

1.5 Motivation: High Operation Performance Organic Transistor

As we know the problems of organic FET, we want to seek the new structure transistors which have the characteristics that can solve the problems of organic FET. Then we search structures of the inorganic semiconductor devices, we found a structure is Metal Base Transistor (MBT) that can solve the problems of organic FET. Metal base transistor has follow characters: Vertical structure, high output current, low operation voltage and high operation speed.

First, the Metal Base structure is vertical structure which compatible to the polymer spin coating processing. The main processes just evaporate metals and spin coat the polymer materials. The output current is not related to the carrier mobility so the output current will not be limited. Second, the operation voltages just need few volts; this is good for commercial application. Final, MBT can be operation in high frequency. The only problem is the current gain in this structure will limit by the quantum-mechanical reflection effect in the inorganic device because the semiconductor is growth by the epitaxial so the interface is perfect in the device. And we think the quantum mechanical reflection effect will not so important because the interface is not as sharp as in the inorganic device. The latest develop of the semi-organic metal base transistor was develop by M. S. Meruvia and I. A. Hummelgen et.in May 2004[4]. The structure is $C_{60}/Au/n-Si$, as the figure 1-2

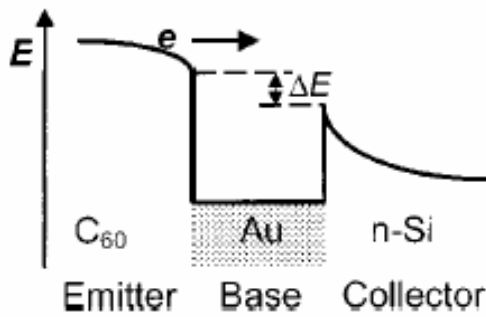


Figure 1-2 Band diagram under bias

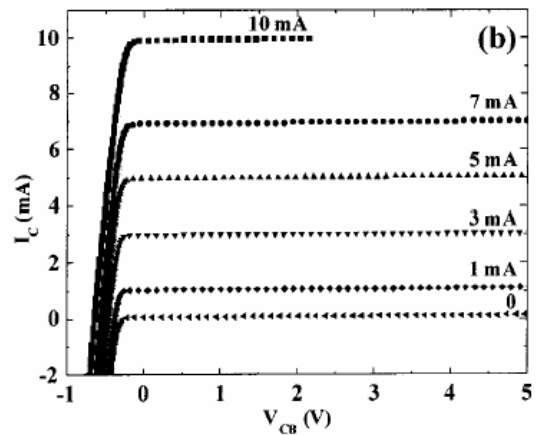


Figure 1-3 Common Base Mode output Characteristic

The output performance is great. The transportation value up to 0.99 ± 0.02 , the current gain β was get by calculating from (1-2)

$$\beta = I_C / I_B = \alpha / (1 - \alpha) \quad (1-2)$$

From the equation they got the current gain about 100 ± 20 . In this device, the quantum mechanical reflection almost can be neglect that means there is almost no hot carrier lost in the base layer. Although the emitter material is organic material but the way to deposit is the thermal evaporation. The cost of depositing organic material of this device was evaporating that is still much higher than deposit in solution processes. The other problem is the substrate in this paper they still use the Si wafer that means the device is non-flexible. But from this result, we trust the all organic high performance metal base transistor is reliable more deeply.

1.6 Organic Electronics Compare with Inorganic Electronics

In fact, it is almost impossible that the device operation performance of organic transistors will higher than the inorganic transistor. But there are some reasons that we need high performance organic transistors. The reasons are low cost, environment resource save and flexible application.

First, the cost of organic transistor is much lower than the inorganic transistor. The main cost of the organic transistor just some processes equipment and those

equipments are less expensive than the inorganic transistors. For example, semiconductor deposit, the equipment is spinner (for spin coating) or mechanical motor (for dip coating) and the environment in the glove box. But for Si, the first equipment is used to make Si single crystal. What is the different? For the spinner, in the lab size the cost about 3000 dollars. The cost of the equipment of making single crystal Si is at least 30000 dollars even higher. But for Si the process does not finish yet, the Si still need to change the properties for different purpose. In short, the cost of organic devices is much less than the inorganic device. So that, for the some application that do not need the perfect operation performance we can chose use the organic devices. For example: portable cell phone.

Second, because the processes of organic devices making are much easier than the inorganic devices. The resource what used in the processes of organic devices making will much less than the inorganic devices making. So that we can waste fewer earth environment and nature resource.

Final, the most attractive reason is the flexible devices. Due to the basic characteristics different, the organic devices can be made on the flexible substrate. For the basic materials difference, organic materials are non-crystal and Si is crystal, when the substrate bending the single crystal will break but organic material will not break. In a word, organic devices are the first chose of flexible application.

There are lots of different kinds of “electronics” are prepare to develop in the future. For example, spin electronics. Due to organic devices have the advantages that are low cost, low cost, environment resource save and flexible application. We believe the high performance organic transistor is an important part in the future.

Chapter 2 Fundamental Theory

2.1 Metal-Base Transistor (MBT)

Metal-Base Transistor (MBT) generally refers to the Semiconductor-Metal-Semiconductor (SMS) structure. This structure was reported in the mid-1980s [5]. This first SMS structure was made by Rosencher et al. and Hensel et al. Although metal base transistor has been developed for more than 40 years. But the device is not matured enough for commercial application. The main problem is the limit of its current gain due to the quantum mechanical reflection.

The real structure is the Si/CoSi₂/Si, which is grown by epitaxy and MBE. The thickness range of CoSi₂ is between 5 and 30 nm. The doping of Emitter and Collector is about 10¹⁶ cm⁻³.

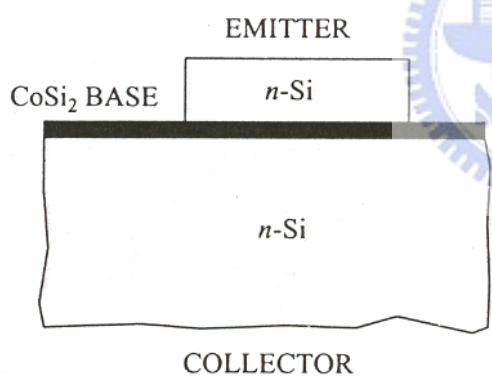


Figure 2-1 Structure of Si/CoSi₂/Si Metal Base Transistor

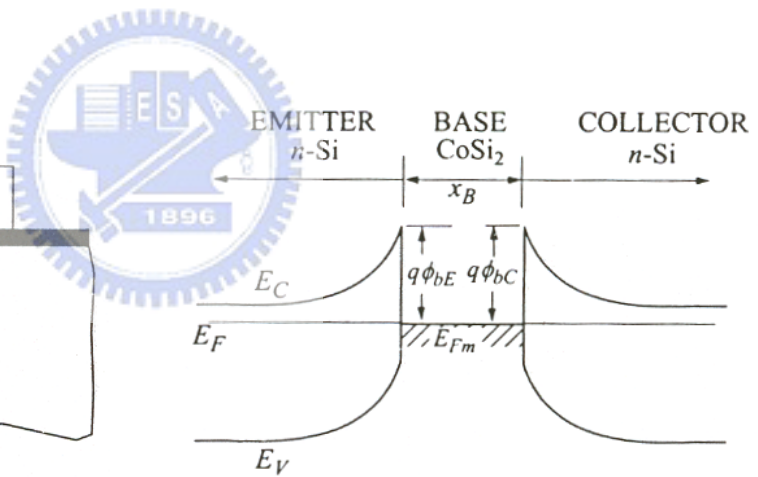


Figure 2-2 Energy diagram of a metal base transistor under thermal equilibrium

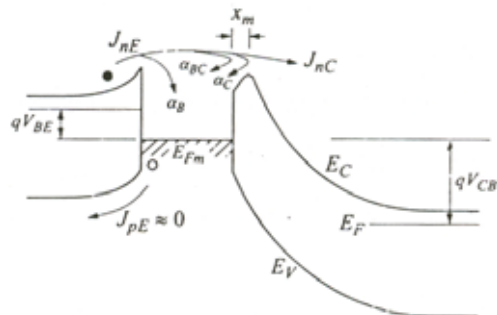


Figure 2-3 Energy band diagram of a metal base transistor under normal bias

In this device, the majority carriers in this structure is due to the thermionic emission and is given by

$$J = \left[A^* T^2 \exp\left(\frac{-q\phi_b}{KT}\right) \right] \left[\exp\left(\frac{qV}{KT}\right) - 1 \right] \quad (2-1)$$

In the figure (Normal Bias), The X_m is the field reversal region from image-force lowering. And the α_B , α_{BC} and α_c are indicate the loss of hot electron. The collector current is given by

$$J_C = \alpha_T J_E \quad (2-2)$$

$$= \alpha_B \alpha_{BC} \alpha_c J_E \quad (2-3)$$

Where α_T is the base transport factor of hot electron. The α_B is due to electron scattering in the metal base, the scattering comes from electron-electron scattering and electron-phonon scattering, given by

$$\alpha_B = \exp(-X_B / l_{mB}) \quad (2-4)$$

Where l_{mB} is the carrier mean free path in the metal base, typical l_{mB} is 10nm at the room temperature. The α_{BC} is due to quantum-mechanical reflection at the base-collector interface, given by

$$\alpha_{BC} \approx 1 - \left[\frac{1 - \sqrt{1 - (q\phi_{bC}/E)}}{1 + \sqrt{1 - (q\phi_{bC}/E)}} \right]^2 \quad (2-5)$$

For a band symmetrical device, this term will approach to zero.

The last term α_c is the collector efficiency that is due to back-scattering of electrons within the distance X_m of the image-force lowering and given is by:

$$\alpha_c = \exp(-X_m / l_{mC}) \quad (2-6)$$

where the l_{mC} is the carrier's mean free path in the collector. The experiment result of common-base output is shown in the Figure 2-4:

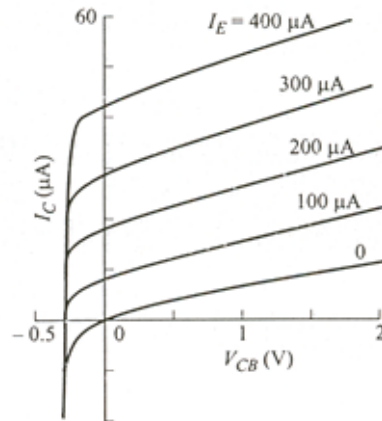


Figure 2-4 Common-base output characteristics of a metal base transistor

2.2 Tunneling Hot Electron Transfer Amplifier (THETA)

The THETA represents a class of hot electron transistors whose emitter injection current is via tunneling through a thin barrier. And the operation principle is the principle of metal base transistor where the difference is the injection current is comes from the tunneling current. There are many different types THETA [7][8], there is one of the structure which is similar structure as the structure the we have in the organic hot hole transistor. The theory current gain is much higher than the metal base transistor. The current gain β values as high as 40 have been reported.

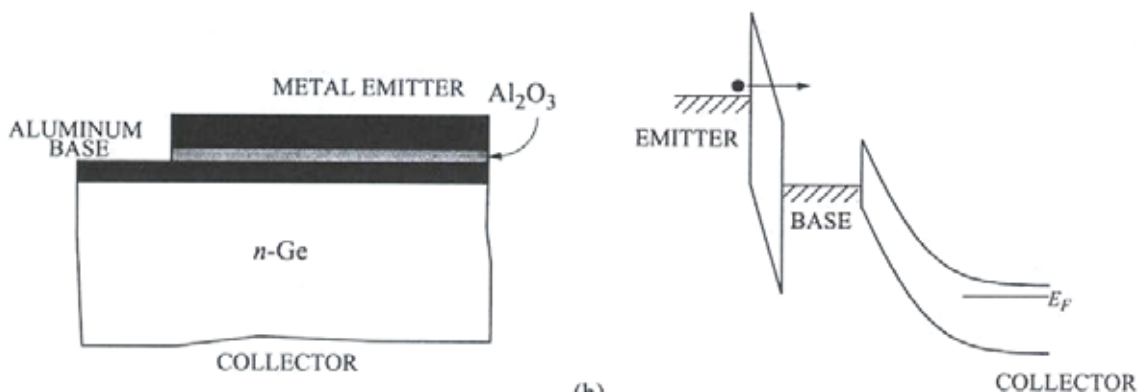


Figure 2-5 the structure and the energy band structure under bias

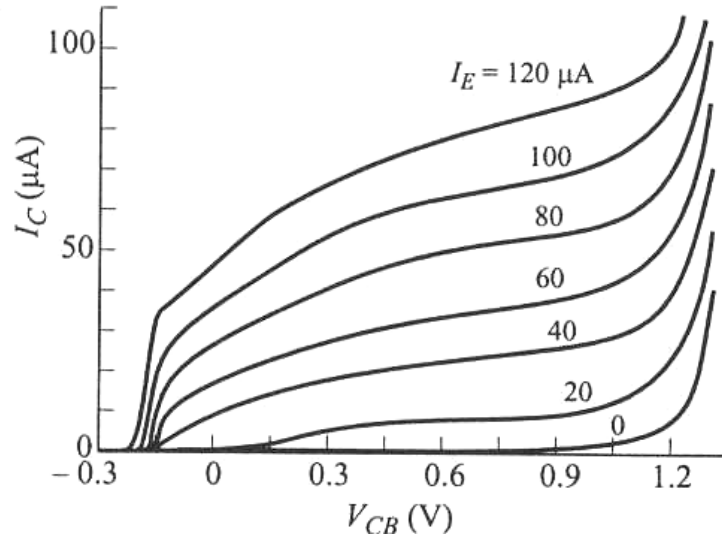


Figure 2-6 The output characteristics of a THETA in the common base mode
2.3 Space Charge Limit Current (SCLC) [9][10][11]

When the metal/semiconductor interface is ohmic contact, there is no barrier block carrier injection or the strong external bias applied the carrier injection do not effect by the barrier of interface, carrier transportation will decided by semi conducting material its transportation characteristics. Due to the carrier inject rate at the cathode is faster than the speed of carrier transport in the material, carrier

The drift current of carrier injection is given by

$$\mathbf{J=qnv} \quad (2-7)$$

The Poisson of the form

$$\frac{d^2 \psi}{dx^2} = \frac{qn}{\epsilon_s} \quad (2-8)$$

$$\mathbf{v = \mu \epsilon} \quad (2-9)$$

In the ballistic regime where there is no scattering,

$$v = \sqrt{\frac{2q\psi}{m^*}} \quad (2-10)$$

The space charge limit current can be shown to be

$$J = \frac{9 \epsilon_s \mu V^2}{8L^3} \quad (2-11)$$

2.4 Hot Carrier in the Base layer

The thickness of the base layer is the most important factor of the hot carrier transistor. The base layer thickness should be less than the hot carrier mean free path of the carrier in the base layer so that we can avoid the carrier collision. But there still have carrier lost machines in the base layer. The hot carriers lost due to carrier-carrier scattering and carrier-phonon collision. [12][13][14]

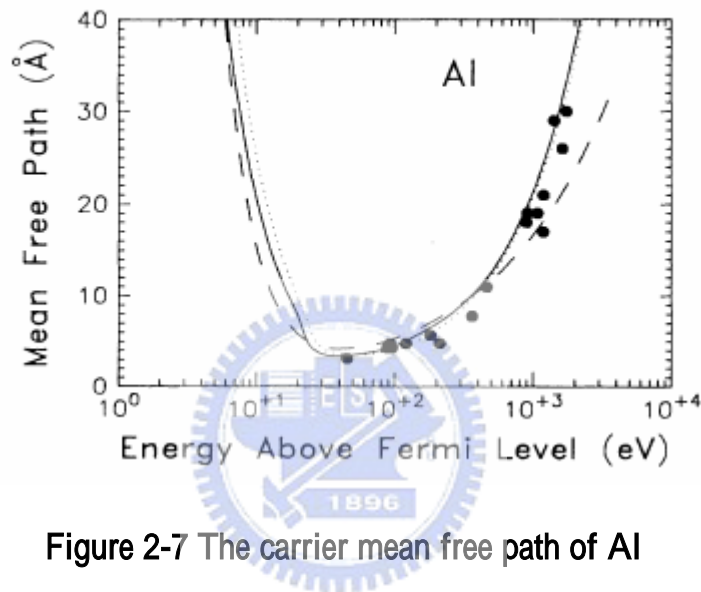


Figure 2-7 The carrier mean free path of Al

2.5 LiF help the hole injection

Recently, more and more PLED will add a thin LiF to help the carriers' injection. The main theory is LiF will make the voltage drop in this layer so that the injection barrier will lower. In the hot hole transistor we are going to use the LiF to enhance the carrier kinetic energy. Make the carriers hotter to reduce the carriers lost in the base layer..

Chapter 3 Experiment

3.1 Introduction

The structure what we made is the Tunneling Hot Electron Transfer Amplifier (THETA), and the structure is shown in the figure 3-1. Figure 3-2 is the device band diagram under normal bias. Due to the LiF is insulator, carriers will pass this layer by tunneling so that the most voltage drop is in this layer. For the electron, there are lots of electron traps in the polymer and in this structure there is a high barrier of electrons. We can make sure this device is a hole only device.

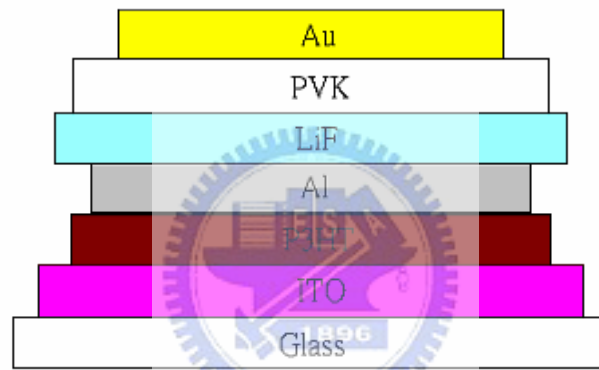


Figure 3-1 the structure of Hot Hole Transistor

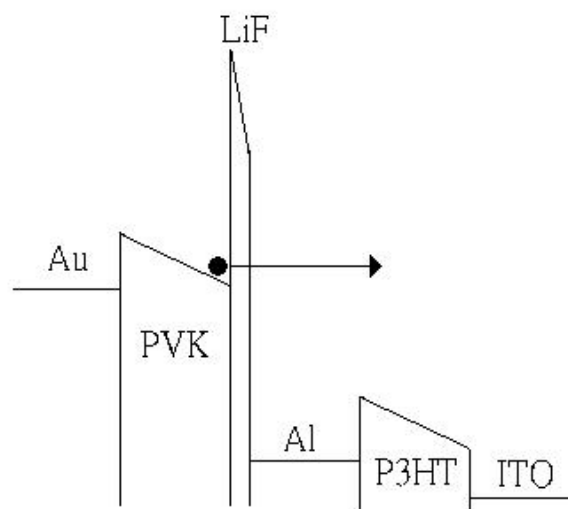


Figure 3-2 Band Diagram of Hot Hole Transistor under normal bias

3.2 Experiment Process

The entire polymers what we use are buy from the Aldich. Then polymers deposited by spin coating. The metal layers are deposited by thermal evaporating. The processes and notes are described as follower:

3.2.1. Pattern Define:

Define the pattern on the commercial ITO glass by the acid etching. The thickness after acid etching is 140nm. The ITO pattern after pattern defined as follower:

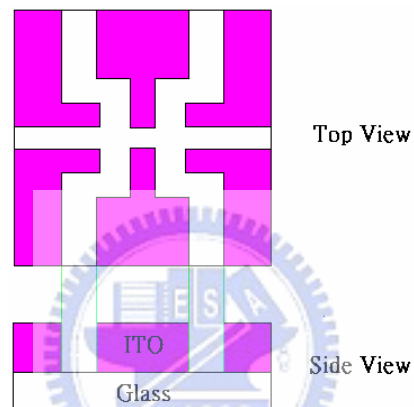


Figure 3-3 The ITO paten

Steps:

- (1) Put the chips in the de ionic water bath with ultrasonic resonance for 20minutes
- (2) Tape the PCB dry film on the dry cleaned chips.
- (3) Exposed the pattern by ultraviolet with the wavelength 365nm through the shadow mask.
- (4) Strip the non-exposed parts by the solution
- (5) Etching the ITO glass by warm HCL solution.
- (6) Clean the chips with DI water
- (7) Clean the exposed parts film with KOH solution.
- (8) Dry the chips with dry N2 gas flow

3.2.2. Clean:

All the chips are clean before deposit the first layer. There are two main step included remove particles, remove organic pollution. The surface must keep clean no particles or the polymer films may become rough. The roughness in the Hot hole transistor is very important because there is a thin base layer will be evaporate on the first polymer.

Steps:

- (1) Put the chips those we needs in the acetone bath with ultrasonic resonance for 5 minutes in order to remove the organic pollution.
- (2) Brush the chips with clean brush and under the DI water current flow in order to remove the particles.
- (3) Put the chips in the IPA bath with ultrasonic resonance for 5 minutes in order to remove the organic pollution again.
- (4) Put the chips in the DI water bath with ultrasonic resonance for 5 minutes in order to remove the solvent
- (5) Dry the chips with dry N₂ flow to blow off the water on the chips.
- (6) Put the chips on the hot plate at 120 degree for 10 minutes to remove the moisture.
- (7) Cool down to the room temperature.

Note: In general PLED clean processes; after clean with organic solvent, there is a step is bath with warm H₂O₂ or expose in the UV-O₃ light. The reasons are to change the ITO work function and change the surface of ITO become hydrophilic. Because in the PLED processes the first step need to deposit a hole transport layer which in general is PEDOT and its solvent is water. But for our structure the surface need to be hydrophobic because the solvent of polymers are organic solvent.

3.2.3. Spin coating collector layer(P3HT)

In this step, we deposit the collector on the patterned ITO glass substrate by spin coating. The material what we deposit is P3HT with molecular weight is 87000. After we spin coating the P3HT film, we need to clean the area where do not need with acetone and the final pattern as figure. Then put the chips in the glass vacuum chamber and put the chamber on the hot plate baking at 120C for 1hr. Finally let the chamber cooling down in the room temperature for 20minutes.

Parameters:

Solution Concentration — P3HT (Mw=87000),1.2%wt chloroform

Film thickness— 1250A

Spin speed and time — One step, 1100rpm for 30s.

Baking — In the vacuum chamber with pressure 5×10^{-2} torr. Put the chamber on the hotplate at 120 degree for 1hour then cool down in the room temperature for 15minutes

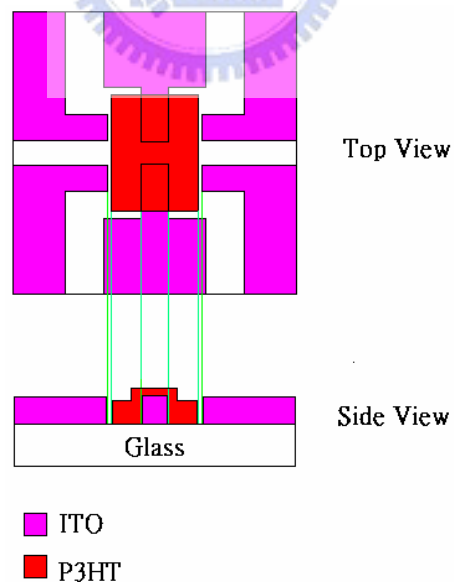


Figure 3-4 P3HT spin coating

Note: When we define the pattern, the gap between the ITO and P3HT is necessary. This gap will avoid the leakage from Collector and Emitter

3.2.4. Evaporate The Al Layer

We evaporate the super thin base layer that the thickness less than the carrier's mean free path so that the carriers can through the base in ballistic way. This step must be control very well or there will not have the transistor characteristics.

Parameters:

Base layer:

Thickness — 100 Å

Evaporate rate — 0.2 Å/s

Chamber pressure — 5×10^{-7} torr

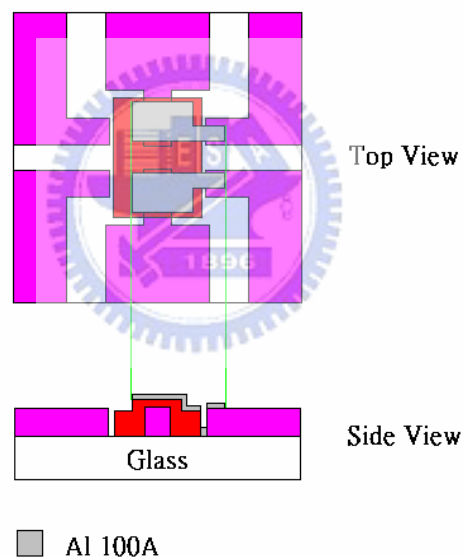


Figure 3-5 Base evaporate

As this figure 3-5 shows that the Al 100Å does not thick enough to cover the steps between P3HT and glass and between ITO and glass. That means the base will break. In order to avoid this condition; after evaporate base layer, we evaporate an contact Al. The figure 3-6 shows the figure after evaporate the contact Al.

Note: the evaporator is in the glove box, the moisture and oxygen is controlled very well. In the glove box the oxygen and moisture value are less than 1 ppm.

Contact Layer:

Thickness — 1000 Å

Evaporate rate — 5 Å/s

Chamber pressure — 5×10^{-7} torr

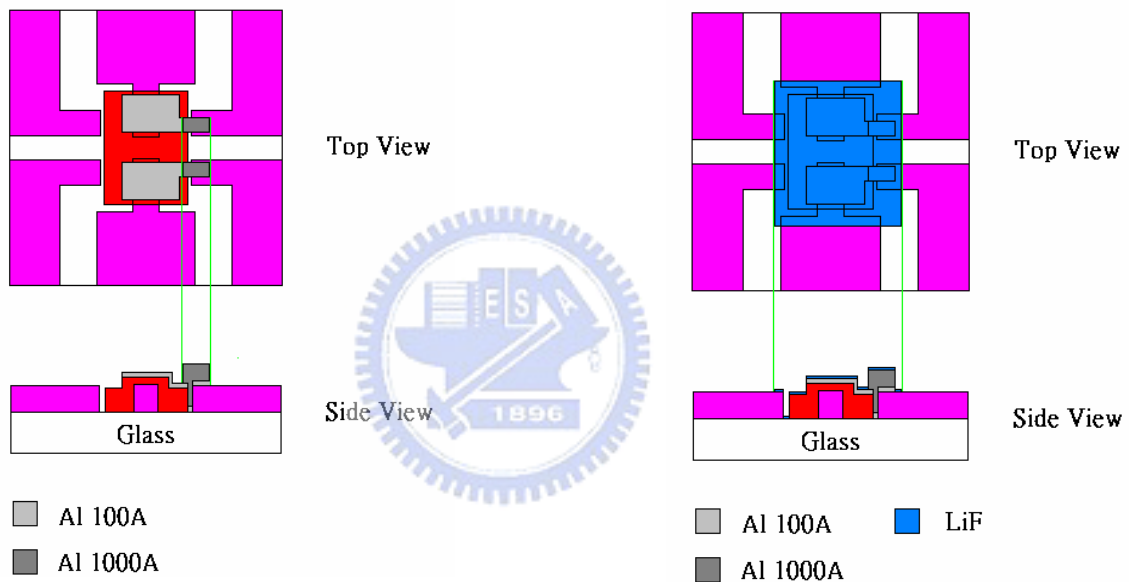


Figure 3-6 Evaporate Contact Al

Figure 3-7 Evaporate LiF

3.2.5. Evaporate the Barrier Layer

In the hot hole transistor structure, we add one LiF layer to help the hole injection and increase the kinetic energy of carriers. There is another function is avoid the polymers mixture with each other.

Parameters:

Film thickness — 30Å

Evaporate rate – 0.2Å/s

Chamber pressure — 5×10^{-7} torr

3.2.6. Spin on the PVK Layer

We spun the emitter layer (PVK) on the chip. The time between drop the polymer solution and push the start bottom must be control very well because if this time too long the solvent will melting the layer of P3HT(Collector), what about too fast, the film will not form very well. After us spinning the PVK, we need to clean the PVK that we do not need. Finally baking the chips in the vacuum holder for 1 hr and cooling in the room temperature for 20mins.

Parameters:

Solution Concentration — PVK ($M_w=84000$), 7%wt toluene

Film thickness— about 3000A

Spin speed and time — One step, 2500rpm for 60s.

Baking — In the vacuum chamber with pressure 5×10^{-2} torr. Put the chamber on the hotplate at 120 degree for 1hour then cool down in the room temperature for 1hour.

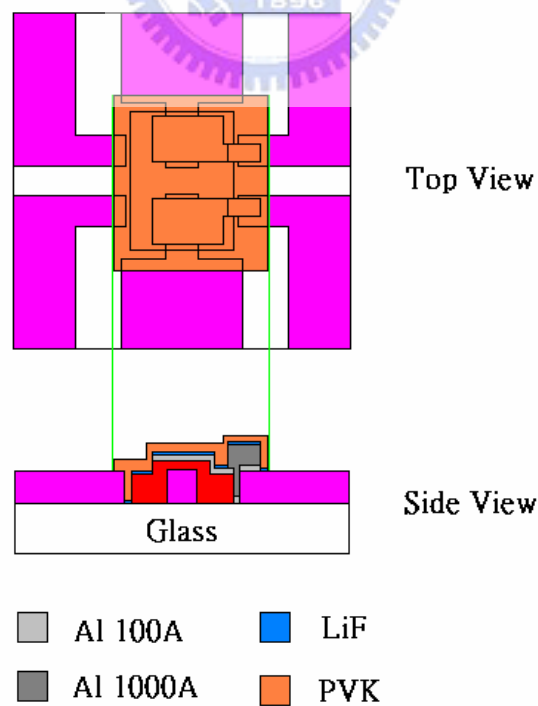


Figure 3-8 Deposit PVK layer

3.2.7. Au cathode

We use thermal evaporator to evaporate the gold as the emitter cathode. In general evaporate parameters we can not get the result what we get because there is a high barrier for carrier injection. In theory, the carriers will injection only when apply high voltage. But in the device what we have did not need to apply high voltage, it is because the evaporated rate is very high and time is short. Due to the gold surface is rough; there are tips on the surface. When we apply voltage, the tips will discharge so that the local voltage will much higher let the carrier injection.

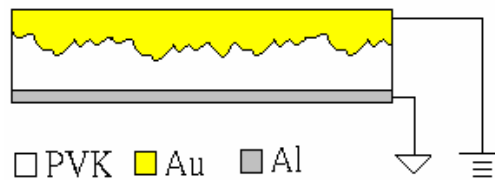


Figure 3-9 The surface of Au

Parameters:

Film thickness — about 1500 Å

Evaporate rate — about 50Å/s

Chamber pressure — 5×10^{-6} mbar

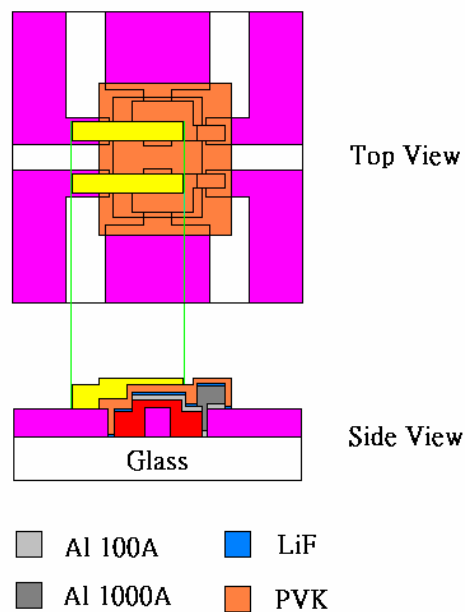


Figure 3-10 Au deposit

3.2.8. Package

Because we want make the device life time longer, we need to package the sample to avoid the oxygen and moisture. In order to protect the sample when we packing the device were in the glove box and when we seal the cap the N₂ gas will in side. We seal the cap by the glue which will be cross link when it exposed under the ultra-violate light for proper time and the wave length is 356nm.

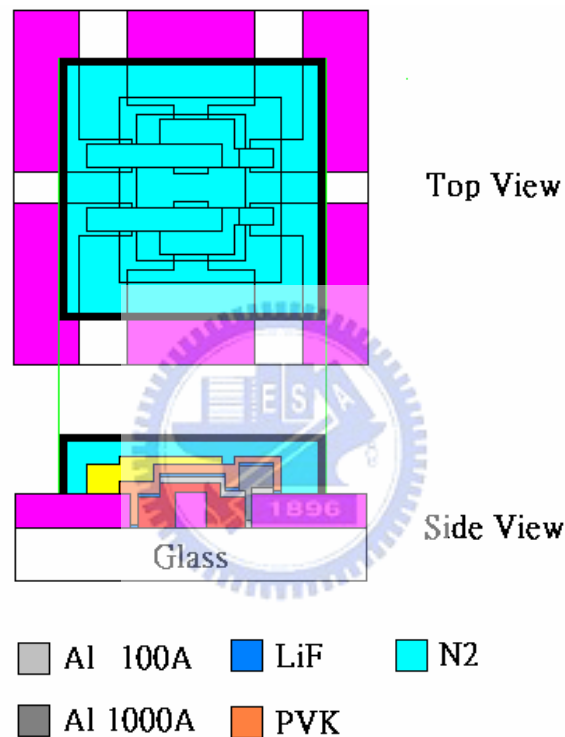


Figure 3-11 Packing

3.3 Measurement processes

3.3.1 Introduction

The data measurement is by the HP4156 semiconductor analyzer, the resolution is higher than 3pA. The measure included checks the device work. The measurements are device check, output characteristics and switching time measurement.

3.3.2 Device check

In our structure, we have two diodes, one is Emitter-Base diode the other is the Base collector. The Emitter-Base diode needs to inject the carrier. So we more care about its forward current. But the hold diode character still very important, it can help us to make sure the interface problem. For the Base-Collector diode, we need to reduce the reverse current which is the leakage of the device. This figure is the diode in the transistor, in the range of voltage operation; we can get very good diode characteristics.

Emitter-Base diode

For this diode, due to the device is operation under the forward bias when we check this diode will mention about the diode forward current. But the reverse current still need to check because it can show out the interface problems.

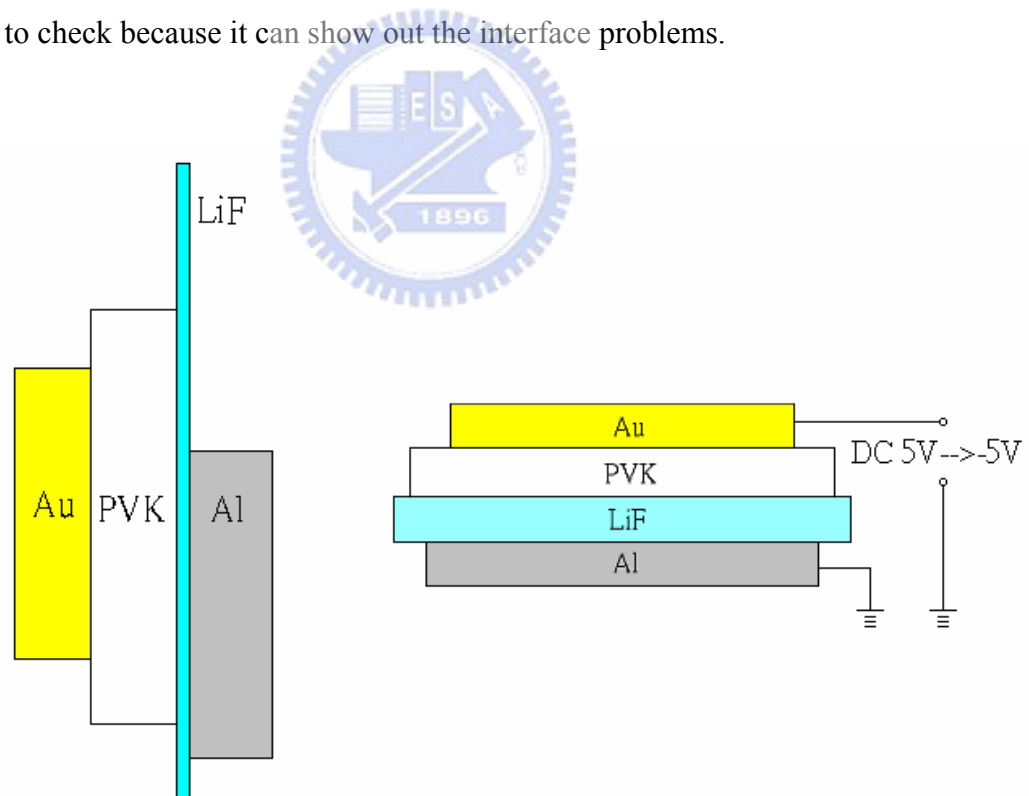


Figure 3-12 Emitter-Base diode measurement

Base-Collector diode

The Base-Collector diode is a very important part of our device which can decide the device output characteristics. In our structure, the Base-Collector is operated at the reverse bias. And the reverse current is the leakage of the device because the output current does not come from the reverse current is come from the hot carrier ballistic transport. The reverse current of device must be as low as possible.

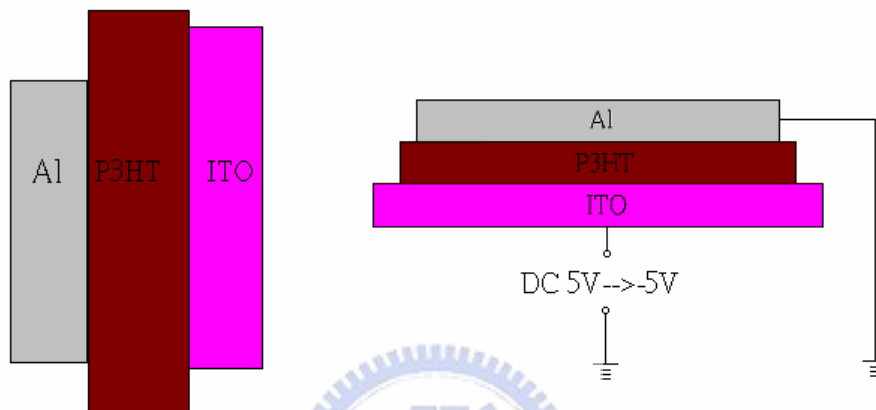


Figure 3-13 Base-Collector Diode

Emitter Collector leakage

Although the leakage is decided by the Base-Collector diode reverse current, there still have another possible leakage from the structure or the process error. So we apply the operation voltage to test the leakage when the device operation.

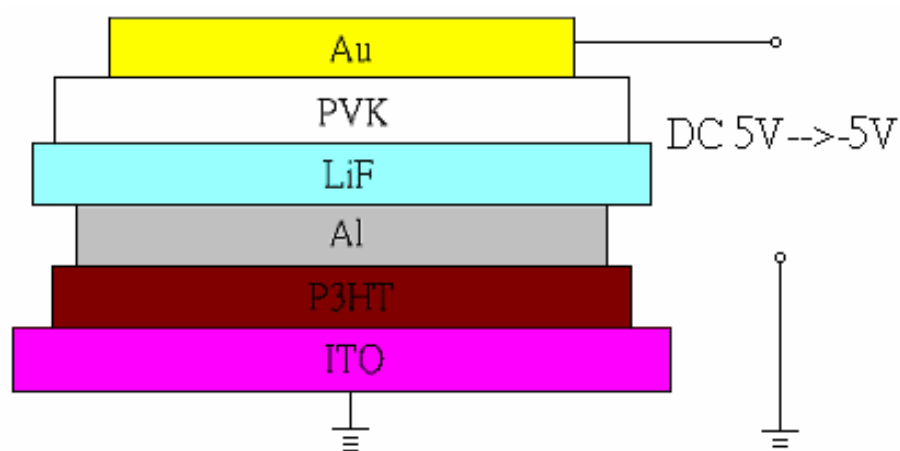


Figure 3-14 Emitter-Collector Leakage measurement

3.3.3 Output Characteristics

Common Emitter mode

This mode is the condition of device operation. Due to the carrier of the device is hole. In this mode, the emitter is grounded. Base offer a static negative current. Under normal bias the emitter-base diode operate in the forward bias. Then scan collector voltage from 0 volt to -5 volts.

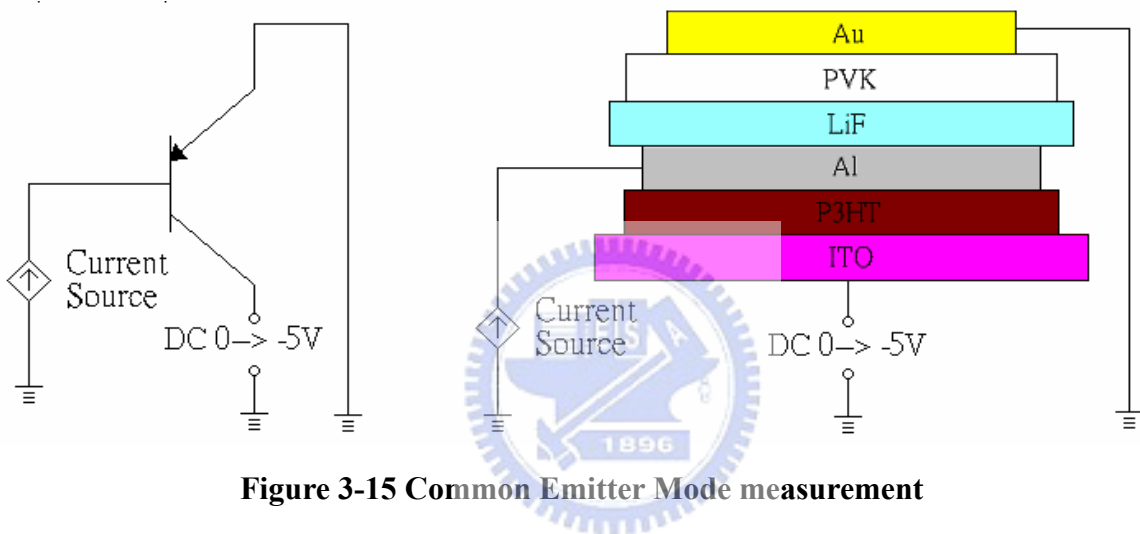


Figure 3-15 Common Emitter Mode measurement

Common Base mode

In this mode base grounded. The emitter injects a static current. Final, scan collector voltage and measure the collector.

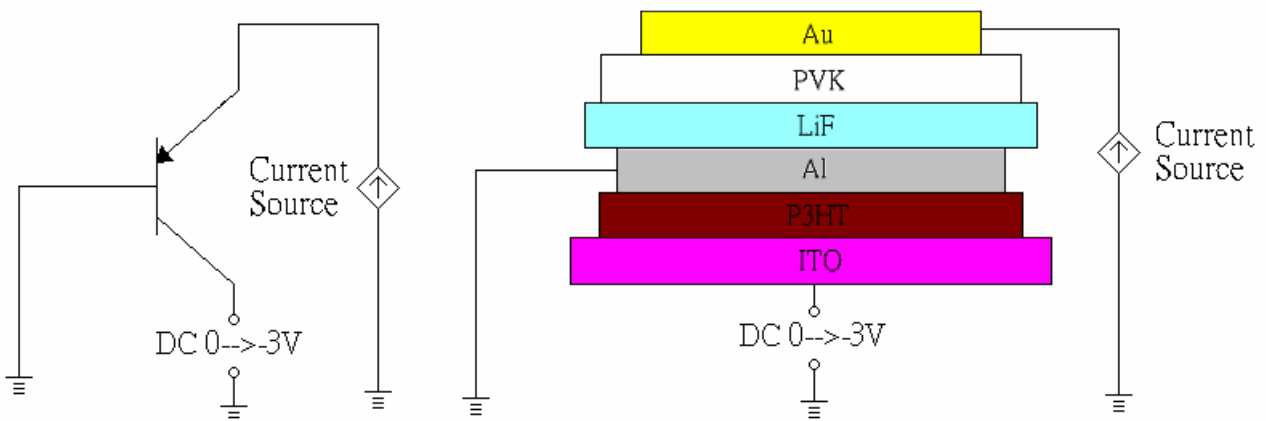


Figure 3-16 Common Base Mode measurement setup

Chapter 4 Data Analysis

Common Emitter Mode:

The common emitter output characteristic is shown in the figure 4-6. First, we calculate the current gain when the voltage is -5 volts the current gain average is 29.33 ± 6.53 . But it is clear that the current gain is not a fix value, that is because the image force lowering. We can fine this when plot the relation of base voltage various with the collector voltage. In our structure, there is a LiF layer which helps the carrier injection and increase the energy different between the emitter and collector. There is another problem which is the leakage of this pixel about few micron amperes. The order of leakage does not the theory expected leakage order. The leakage should be comes from the structure leakage.

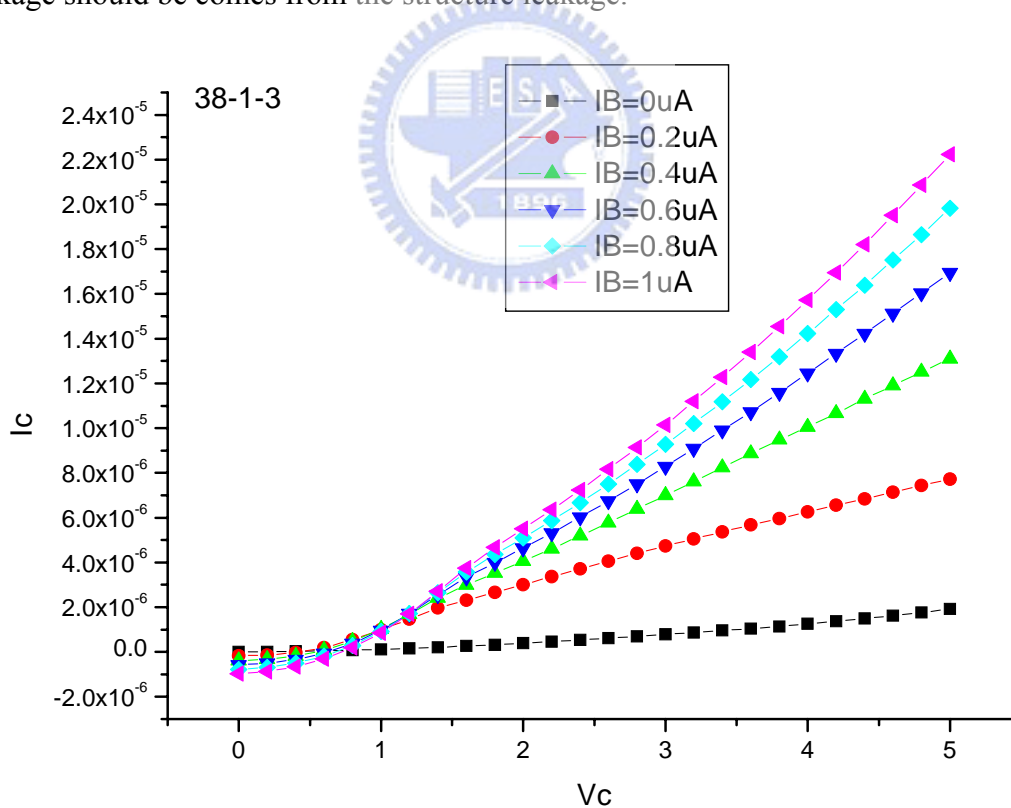


Figure 4-1 Common Emitter Mode Data of 2004.10.14

Common Base Mode

In this mode, we can observe the transport behavior. And the transport factor $\alpha = 1.001 \pm 0.0011$. In this mode, emitter injection current into the collector

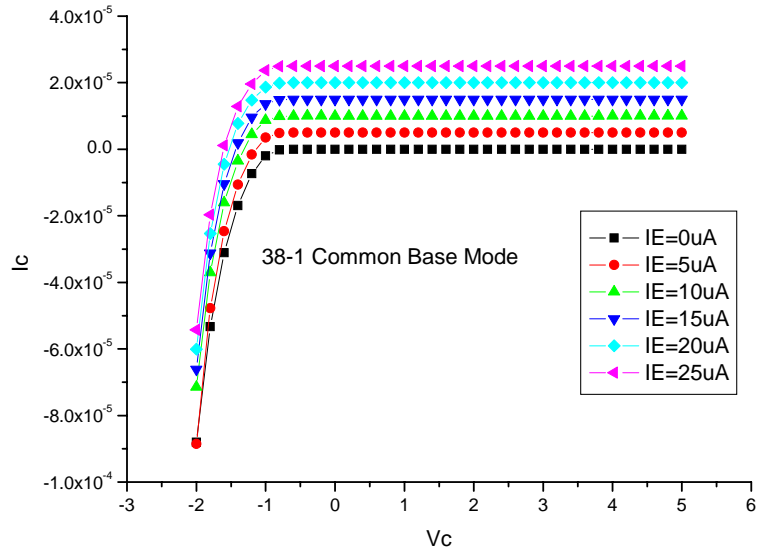


Figure 4-2 Common Base Mode Data of 2004.10.14

Emitter-Base diode

We check the forward current because this part determined the injection current order and the diode behavior will help us to determine the interface condition.

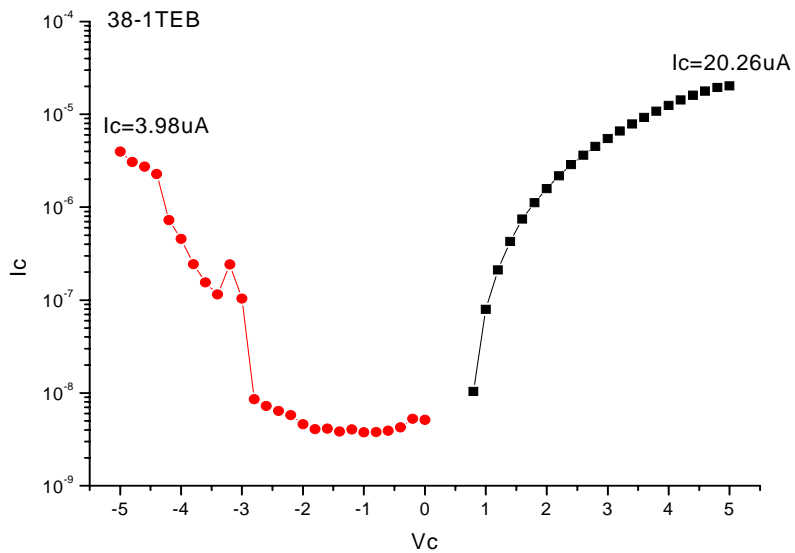


Figure 4-3 Base-Collector Diode

Base-Collector Diode

The Base-Collector diode we will mention about the reverse current because this part will decided the device leakage order. The leakage order should be less than the order of Base-Collector diode reverse current order.

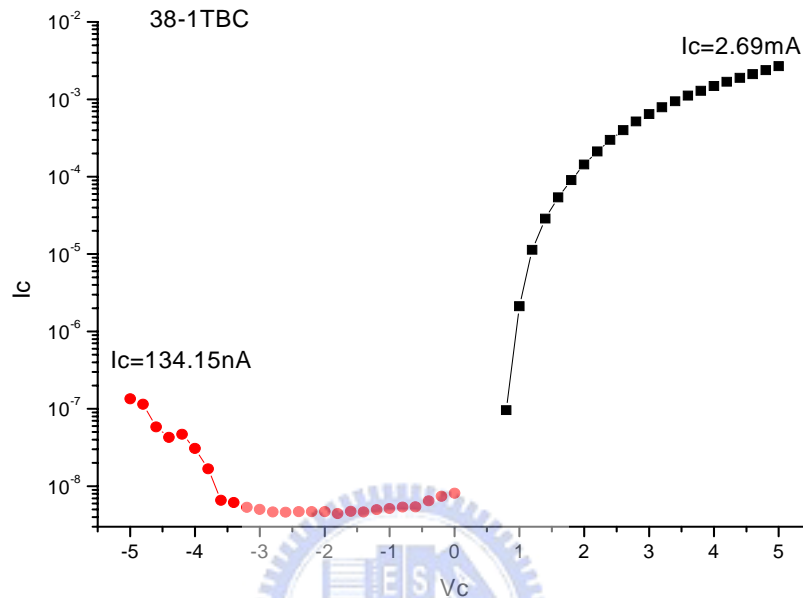


Figure 4-4 Base-Collector Diode

Emitter-Collector Leakage

This will decided the leakage current when the device operation. This device leakage maximum about 2 nA and the average leakage current less than 0.5 nA .

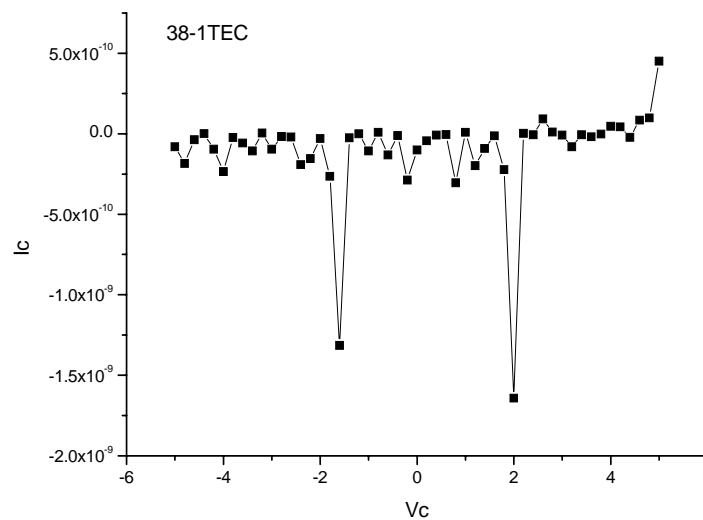


Figure 4-5 Emitter-Collector Leakage

Chapter 5 Conclusion

Our result demonstrated the first polymer hot carrier transistor on the glass substrate. Moreover, the current went up to 29.33. Also, this device has nice output characteristics. The most important thing is that the transportation factor closes to 1. That means if there is enough carrier injection, the current gain can be achieved to the commercial level. However, the process of increasing carrier injection is not easy to control. In the future, there are two main issues of hot hole transistor to be solved. The first one is to increase the injection current and the second one is to reduce the device leakage.



Reference

- [1] STEPHEN R. FORREST, "The path to ubiquitous and low-cost organic electronic appliances on plastic" *Nature* 428, pp. 911 - 918 ,29 April 2004.
- [2] [L. P. Ma](#), [J. Liu](#), [Y. Yang](#), "Organic electrical bistable devices and rewritable memory cells" ,*Applied Physics Letters* ,Volume 80, Issue 16, pp. 2997-2999, April 2002.
- [3] Natalie Stutzmann, Richard H. Friend, Henning Sirringhaus "Self-Aligned, Vertical-Channel, Polymer Field-Effect Transistors", *Science*, Vol 299, Issue 5614, 1881-1884 , March 2003.
- [4] [R. Parashkov](#), [E. Becker](#), [S. Hartmann](#), [G. Ginev](#), [D. Schneider](#), [H. Krautwald](#), [T. Dobbertin](#), [D. Metzdorf](#), [F. Brunetti](#), [C. Schildknecht](#), [A. Kammoun](#), [M. Brandes](#), [T. Riedl](#), [H.-H. Johannes](#), [W. Kowalsky](#), "Vertical channel all-organic thin-film transistors", *Applied Physics Letters* ,Volume 82, Issue 25, pp. 4579-4580 ,June 2003.
- [5] [M. S. Meruvia](#) , [I. A. Hümmelgen](#) , [M. L. Sartorelli](#) , [A. A. Pasa](#), [W. Schwarzacher](#), "Organic-metal-semiconductor transistor with high gain" *Applied Physics Letters* ,Volume 84, Issue 20, pp. 3978-3980, May , 2004.
- [6] [J. C. Hensel](#), [A. F. J. Levi](#), [R. T. Tung](#), and [J. M. Gibson](#) , "Transistor action in Si/CoSi₂/Si heterostructures", *Applied Physics Letters* ,Volume 47, Issue 2, pp. 151-153 July 1985.
- [7] [N. Evers](#), [J. Laskar](#), [N. M. Jokerst](#) , [T. S. Moise](#), [Y.-C. Kao](#) , "Direct current and high frequency performance of thin film InP-based tunneling hot electron transfer amplifiers", *Applied Physics Letters* ,Volume 70, Issue 18, pp. 2452-2454 ,May 1997.
- [8] [T. S. Moise](#), [Y.-C. Kao](#), [A. C. Seabaugh](#) , "Room-temperature operation of a

tunneling hot-electron transfer amplifier”, Applied Physics Letters, Volume 64, Issue 9, pp. 1138-1140 February 1994.

- [9] [Z. Chiguvare](#), [J. Parisi](#), [V. Dyakonov](#),”Current limiting mechanisms in indium-tin-oxide/poly3-hexylthiophene/aluminum thin film devices”, Journal of Applied Physics ,Volume 94, Issue 4, pp. 2440-2448 ,August 2003.
- [10] [S. C. Jain](#), [W. Geens](#), [A. Mehra](#), [V. Kumar](#), [T. Aernouts](#), [J. Poortmans](#), [R. Mertens](#),[M. Willander](#) ,”Injection- and space charge limited-currents in doped conducting organic materials”, Journal of Applied Physics, Volume 89, Issue 7, pp. 3804-3810 ,April 2001.
- [11] [V. R. Nikitenko](#), [H. Heil](#), [H. von Seggern](#) .”Space-charge limited current in regioregular poly-3-hexyl-thiophene” Journal of Applied Physics, Volume 94, Issue 4, pp. 2480-2485, August 2003.
- [12] David R. Penn,” Electron mean-free-path calculations using a model dielectric functions”, Phys. Rev. B 35, pp.482–486, January 1987
- [13] N. G. Ptitsina, G. M. Chulkova, K. S. Il’in, A. V. Sergeev, F. S. Pochinkov, E. M. Gershenson. M. E. Gershenson ,”Electron-phonon interaction in disordered metal films: The resistivity and electron dephasing rate”, Phys. Rev. B 56, pp.10089–10096 , October 1997.
- [14] I. Campillo , V. M. Silkin , J. M. Pitarke , E. V. Chulkov , A. Rubio, P. M. Echenique,” First-principles calculations of hot-electron lifetimes in metals”,Phys. Rev. B 61, pp.13484–13492 ,May 2000.

Appendix A: The Measurement Items that we need to Measure

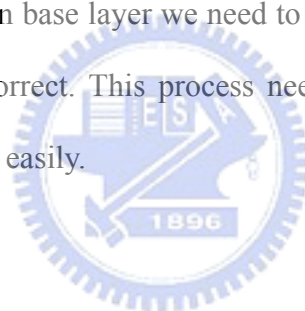
Because there are lots of problems we have during develop the Polymer Hot Hole Transistor, there are some measurement note that we need to measure to make sure the process and the parameters is correct. I list as follow:

A.1 ITO paten check:

After we defined the paten on the ITO, need to measure the leakage between the cathodes.

A.2 the Base resistances check

After we evaporate the thin base layer we need to measure the sheet resistances to make sure the thickness is correct. This process need to measure in the glove box because the Al wills oxidation easily.



A.3 Diode check

This is the basic device characteristic to make sure the device can work or not. Do not apply high voltage that will make the device broken.

A.4 Leakage check

Make sure the leakage order when device operation.

A.5 Common Emitter Mode

This is the device operation mode. After apply the base current form low to high, for example: from 0nA to 100nA, apply the base current in the reverse sequence that means from high to low, for example from 100nA to 0nA. The purpose to reverse the

sequence is to make sure the device does not have memory effect.

A.6 Common Base Mode

This mode is to determinate the current injection behavior. The same as the A.5, need to reverse the Emitter current apply sequence.

A.7 Switching Time

Do not mix with the response time. This is to determinate the switching time when it operation.



Appendix B: The trouble shooting of process of hot hole transistor

During this experiment we met lots of mistakes. These mistakes will not help researcher to improve device performance. But will help the researcher to find the problems rapidly and how to solve to reduce the cost and time of researching process.

1. Step Covering

In the Polymer Hot Hole Transistor, the process has a big point need to mention about is the step covering. Due to the polymer layers thickness are micro meter orders. So those, the contact are some time will broken. There are some situation and the perhaps reason come from the step covering problems.

(1) The Emitter diode only have few nano ampere current output and the the Base diode the same with Emitter characteristics. In this situation, if to measure the common emitter characteristics in the high voltage region there will be have the characteristics as the follower. In this situation, the current gain close to infinity because we need almost zero base current but this is due to the memory effect.

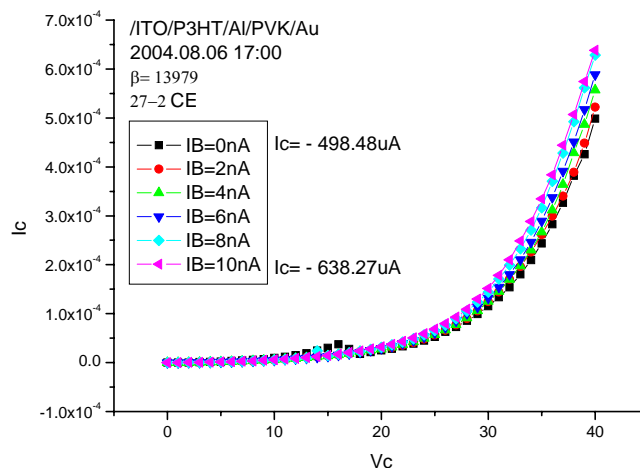


Figure B-1 The memory effect

→ Should be the base too thin or contact Al do not cover partially P3HT layer region

(2) Only Base diode is work and Emitter only have few nano ampere current output.

→Should be the Au layer too thin, make sure the thickness more than 50nm.

(3) Both Base diode and Emitter diode can work but the Emitter-Collector have high leakage current (much higher than the Base diode reverse current)

→Should be the ITO paten does not etching well so that there are some parts are short. This can be solve by checking the ITO paten leakage.

2. Evaporate

In the metal base transistor, the more difficult part is to control the base layer. And for our structure, the Au evaporate conditions will decided the injection current order. So these two parts' parameters must be control very careful and exactly.

(1) Base evaporates:

Due to us need very thin Al layer, the cleaning and vacuum level need keep very well. The evaporate rate as low as possible. Then we need to change the evaporate the shadow mask to evaporate the contact Al, make sure all the processes are in the glove box before we evaporate the contact Al layer.

(2) Au evaporates:

Because of the emitter current injection need to overcome a high barrier, we evaporate the Au film in very high evaporate rate to make tips in the PVK layer to produce localize high voltage. But the condition is difficult to control, we need to make more sample to make sure to get the sample. In the other words we have low yield. The better way to enhance the yield is to control the evaporate parameters carefully. The better condition we found are evaporating in the high evaporates rate and short time. The short evaporate time better because the heat produce by the boat will enhance the Au moving deeply make the device short.

3. Powder problems:

Although the polymers powder what we use is commercial goods. Most polymers brought from Aldich. But there still have some different between two polymers that brought at different. For example: there are polymer 1 and polymer 2. The two polymers are the same type but the molecular weights have few different. The recipe of polymer 1 may not suit for polymer 2 because of the difference of molecular weights. There are some thing need to check to avoid this condition:

- (1) Check the data sheet carefully.**
- (2) Making a standard sample.**
- (3) Retry the parameters of the new powder.**

