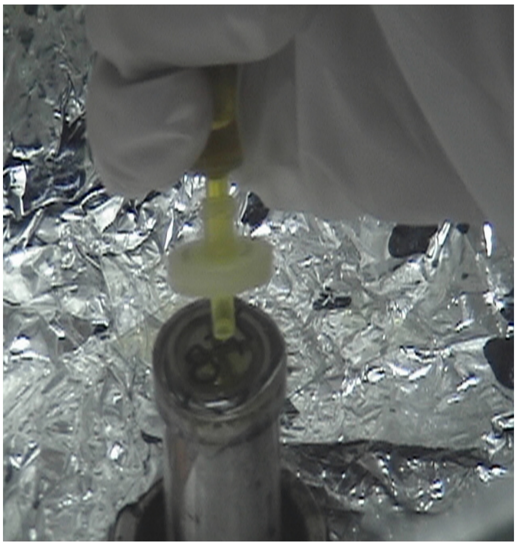

Figure 2.10: At the moment the thin glycol layer is contracting, and the spinner stops rotating, we immediately drop cast the second layer.

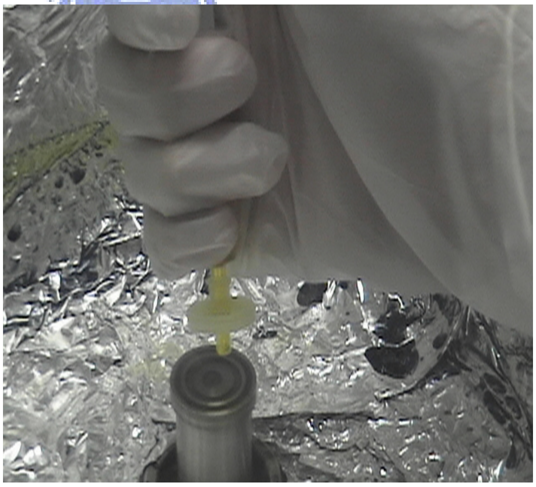

Figure 2.11: After all the processes are done, we resume rotating before the thin glycol layer completely contracts.

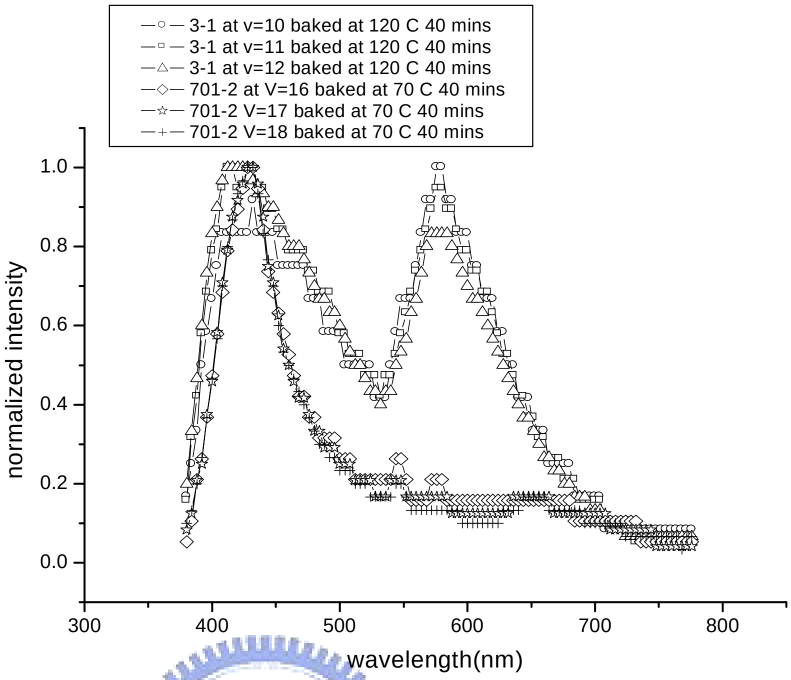

Figure 2.12: A wrong baking temperature could result in wrong spectra. In this case, baking the PVK-PBD blend at 120°C would make it emit 580-nanometer light, which is undesirable.

In our case, we baked the second layer, when it was LEP, at 80°C for 60 minutes. The baking temperature is not suggested to change because if baked at higher temperature, for example 120°C, the PVK-PBD blend would emit differently. See Figure 2.12. When baking at 70°C, however, it emits the same color as expected.

The long baking time was used because we suspected that glycol needed longer time to be baked out under the LEP layer.

Although the theory sounds easy to produce double or triple layer devices, it is in practice very difficult to control this technique and to create uniform films. Figure 2.13 shows some successful bi-layer samples and some failed ones.

2.5 Removing unwanted parts with Acetone.

After spincoating, the sample is cleaned with acetone to remove the polymer layer(s) almost everywhere from the sample, except for the region in

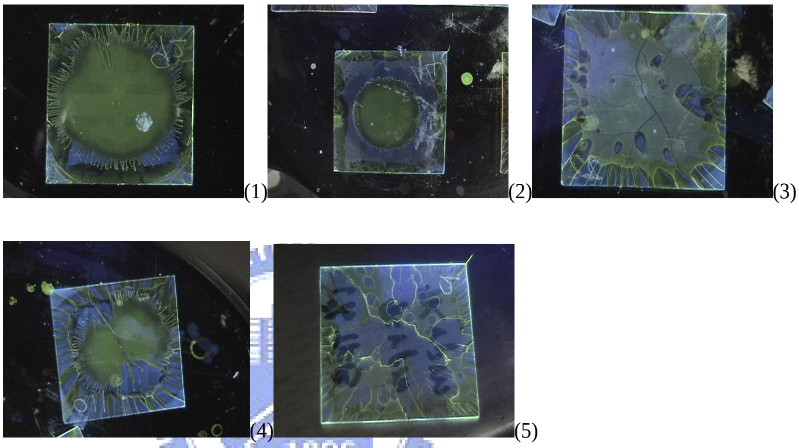

Figure 2.13: Successful double-layer samples and failed ones. (1) and (2) show devices after successful buffer-layer treatment. The circle at the middle emits green (LEP photoluminescence) while the background emits blue (TFB photoluminescence). They separated distinguishably. (3) and (4) show semi-successful devices after the treatment. Some active areas were covered by the green-emitting LEP layer while others are not. There are also some holes on the green parts. (5) shows a failed device. We can see that the second green layer raggedly spreads over on the surface.

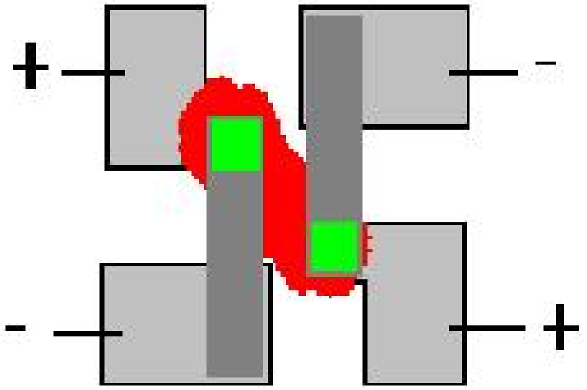

Figure 2.14: Removing unnecessary part by acetone, leaving the red part behind as shown in the figure.

the middle in which the active areas are located. Here are the two PLEDs themselves, the rest is just to have electrodes to apply voltage. This is also the reason of the etching of the ITO. Figure 2.14 shows the layout of the sample after acetone treatment and cathode evaporation.

2.6 Thermal-evaporating the cathodes.

After removing the unnecessary part on the substrate with Acetone we carry the sample into the glove box. The cathodes (for example Aluminum), together with the insulating layer (for example Cesium fluoride or Lithium fluoride) between the emissive layer and the cathode, are evaporated onto the substrate under vacuum. The substrates are put into a mask that covers the substrate's area on which we do not want any metal to be deposited. Beneath the substrates, a boat with a metal slab or an insulating material is installed. The environment is then pumped into high vacuum (around 10^{-6} Pa). By allowing a current through the boat, the boat heats up and the target material melts and evaporates, going straight from the boat to the substrate due to the vacuum. The deposition rate can be controlled by controlling the current through the boat. This process is the same for any other material that can be deposited. On the other hand, we may get Cesium fluoride by spin-coating a solution which contains Cesium fluoride as the solute and glycol as the solvent.

It is interesting to recognize the effects of the insulating layer between the emissive layer and the cathode. With some proper thickness of it, the device efficiency will be improved astonishingly. Theories regarding to the reasons for efficiency improvement are divided into two different mechanisms. The first mechanism states that the insulating layer tilts the band gaps of the materials on both sides, leading to a much smaller barrier for electrons to inject. The other mechanism is that the two elements in the compound in the insulating layer will separate from each other. For example, the Cesium fluoride will dissolve, after an external applied voltage, into Cs and F_2, the former flying towards the anode while the latter to the cathode. After this, the F_2 flowing to the cathode will interact with the metal (for example, Aluminum). The net free energy of the two reacting processes can then be calculated as following [17]:

$CsF \rightarrow Cs + \frac{1}{2}F_2$, with dissociation energy 125.6 kcal/mol.

$Al + \frac{3}{2}F_2 \rightarrow AlF_3$, with the binding energy -342.3 kcal/mol. Therefore we get the net free energy for the reaction $Al + 3Cs \rightarrow AlF_3 + 3Cs$ to be about 34.5 kcal/mol. With proper combinations of the insulating layer and the metal for the cathode, we may acquire lower net free energy. For example, if we choose Calcium as the metal, the net free energy for the total reaction $\frac{1}{2}Ca + CsF \rightarrow \frac{1}{2}CaF_2 + Cs$ is about -14.9 kcal/mol. Smaller net free energy indicates better electron injection, thus resulting in higher current density. In chapter 3, we will show that current of devices with the combination of CsF/Ca/Al is higher than that of devices with the combination of CsF/Al. However, this does not lead to better device efficiency. As a matter of fact, the efficiency of devices with CsF/Al is shown, at least in the case of our light-emitting layer, to be better than that of devices with CsF/Ca/Al. Moreover, we do not guarantee that, for all the other light-emitting layers which are different from ours, the combination of CsF/Al will always be better than that of CsF/Ca/Al. The emissive layer should play a certain role in the process of chemical reaction, as the metal at the cathode interacts with Fluorine. We postulate that Cs should react with the emissive layer, and this reaction also has a kind of free energy. This could be written as $xCs + yEML \rightarrow Cs_xEML_y$. Further research should be carried out on this point.

2.7 Packaging and measuring of the devices

After thermal-evaporating the insulating layer and the cathode, we package the sample with a smaller piece of glass in the glove box under nitrogen environment. This includes applying the transparent packaging adhesive around the small glass, covering it on our sample, and exposing the sample to UV light for 40 seconds. After exposure, the packaging adhesive holds together the two pieces of glass. The active areas between them are then

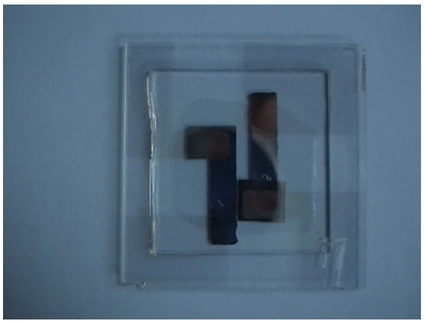

Figure 2.15: A packaged device.

protected. A packaged device looks like the one in Figure 2.15.

To measure the performance of devices we connect Kaithley 2400 and a voltage supplier to a Labview-controlled software. After applying voltages to the device, we get response of current in unit of mill-ampere (hence the current density in unit of milli-ampere per centimeter square), luminance in unit of candela per meter square, yield in unit of candela per ampere, and finally power conversion efficiency in unit of lumen per watt. The definition of the power conversion efficiency is the lumen emitted by the LED devided by power we supply to the device. Be aware not to be confused with the definition of luminous flux defined as the lumen devided by power radiated by a bulb. We also get electroluminescence spectra at each voltage. Generally the spectra are independent of applied voltages. We also get CIE (1931) coordinates, radiance, and bandwidth, which are not important throughout our discussions.

We may conclude the production processes with the chart in Figure 2.16 and conclude the process of spin-coating organic films in Figure 2.17.

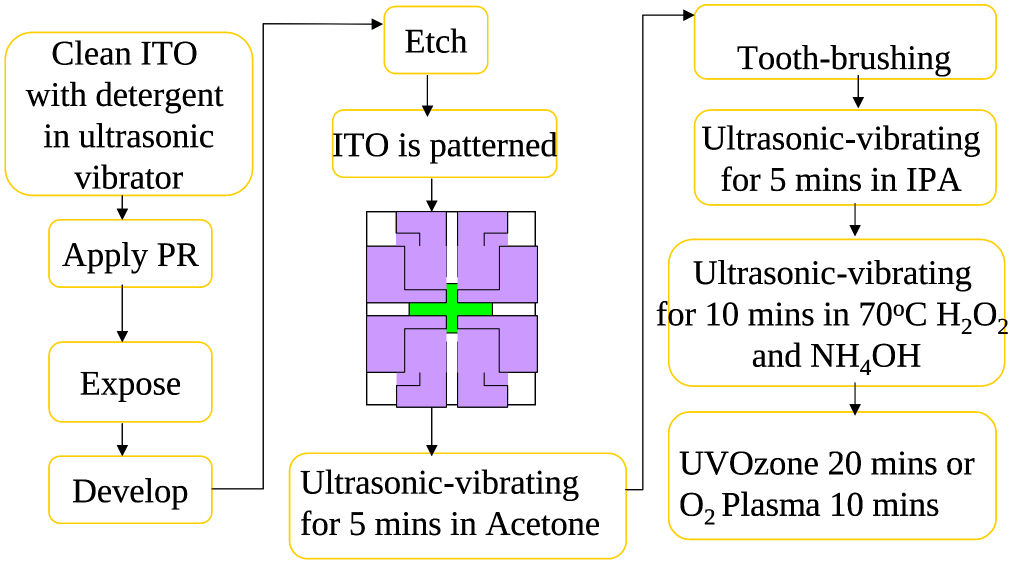

Figure 2.16: The cleaning process of ITO substrates.

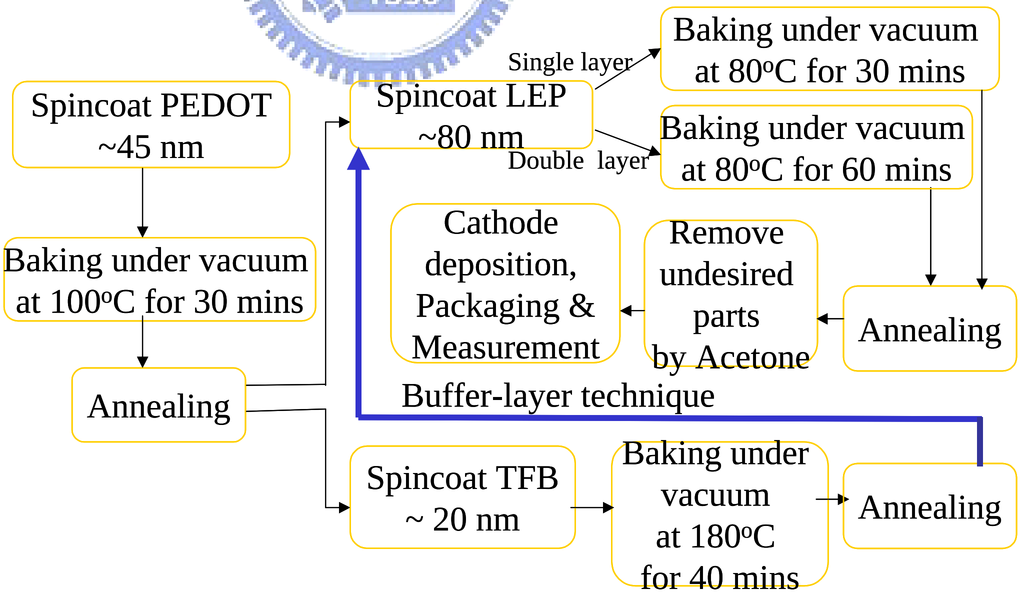

Figure 2.17: Spin-coating organic films.