
2. Fabrication Process for Devices

2.1 Etching for ITO patterns.

ITO (Indium Tin Oxide) is a transparent conducting material. It is always coated on a glass substrate. We need to etch the ITO throughout a process to get the pattern we want. A general photo-patterning is shown in Figure 2.1

First a layer of photoresistor is applied onto the ITO substrate. This substrate is then put into a mask, which covers the parts of the sample where the ITO should be removed. The mask is exposed to UV light for 62 seconds, which hardens the photoresistor. The non-exposed parts are still soft and can now be removed with dissolved NaCl. The ITO is now exposed on these parts and covered with a hard photoresistor layer on the parts that should not be removed. With a bath into HCl, the uncovered ITO is etched away. Finally the hard photoresistor is removed with dissolved NaOH. Two kinds of ITO patterns that are used in our experiments are shown in Figure 2.2 and 2.3.

2.2 Preparations for the solutions

The most commonly used solution in the work was the blend of PVK, PBD, TPD, and Ir(mppy)₃ with the ratio of $PVK : PBD : TPD : Ir(mppy)_3 = 61 : 24 : 9 : 6$ as described in the literature. The solvent was Chlorobenzene with the chemical structure in Figure 2.4.

We prepared the solution in the following way, although it was sometimes questioned of the accuracy of the ratios among the solutes. First we put all the solutes in one bottle with the order of Ir(mppy)₃, TPD, PBD, and finally PVK (from the least to the most). Secondly we added the solvent, Chlorobenzene, to make the solution up to a desired total concentration. The total concentration is defined as the weight of all the solutes divided by the total weight of the solution. Typically, we usually added 61 milligrams of PVK, 24 milligrams of PBD, 9 milligrams of TPD, and 6 milligrams of Ir(mppy)₃. The total weight of all the solutes was usually about 100 milligrams. Afterwards we usually added 3233.3 milligrams of Chlorobenzene to make the total concentration of the solution to be about 3 per cent.

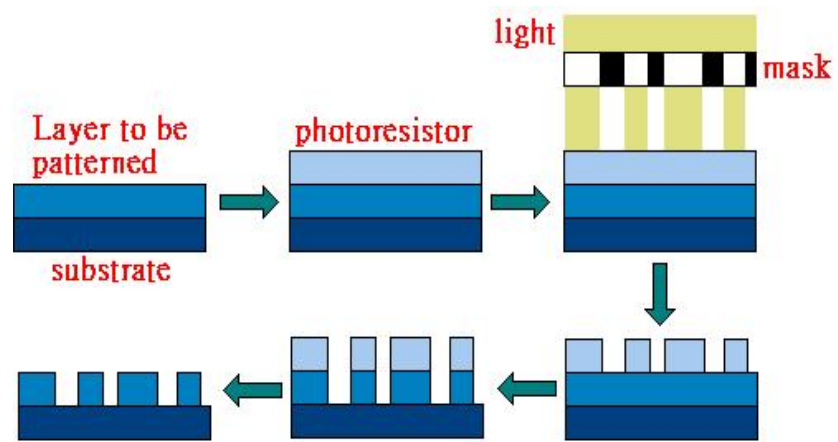


Figure 2.1: Schematic description of photo patterning of our ITOs.

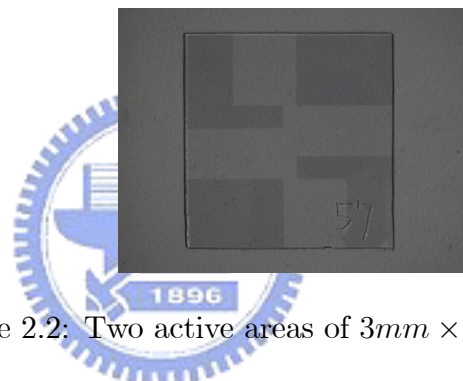


Figure 2.2: Two active areas of $3\text{mm} \times 3\text{mm}$ for each.

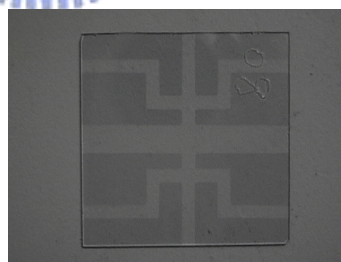


Figure 2.3: Four active areas of $2\text{mm} \times 2\text{mm}$ for each.

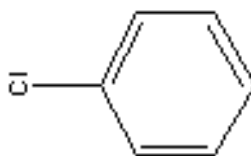


Figure 2.4: The chemical structure of Chlorobenzene. It consists of Benzene and Chlorine.

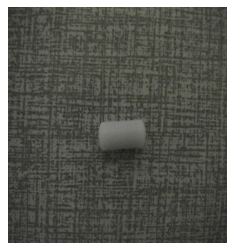


Figure 2.5: A 1-centimeter magnetic stirrer.

At the first glimpse the solutes did not seem to dissolve very well in the solvent. But be patient. Empirically we put one or two 1-centimeter magnetic stirrers, which looks like the one in Figure 2.5, in the bottle containing the solution.

This was a very important step. Stirring the solution on the magnetic stirring machine makes the solutes dissolved much more quickly. Experiences showed that the results of the solution treated with the magnetic stirrers were much better than those of the solution treated with the ultrasonic cleaner. More importantly, one should not heat up the solution if he found at the first look that the solutes were not well dissolved.

2.3 ITO cleaning process.

After etching the ITO, but before any polymers are spincoated onto the substrate, the substrate is thoroughly cleaned. This is done by successively soaking in acetone, flushing with water, brushing with a toothbrush, drying with a nitrogen gun, soaking in propanol, flushing with water, soaking in boiling water mixed with NH_4OH and H_2O_2 , flushing with water and drying with a nitrogen gun. The soaking will be done in an ultrasonic cleaner, which causes microvibrations to clean the surface better.

Since the first layer to be spincoated is typically PEDOT, which is dissolved in water, the ITO surface will be made more hydrophilic by exposure to an ozone producing UV source for 20 minutes or by exposure to oxygen plasma for 10 minutes. Sometimes we used both of them. Exposing to UVOzone or oxygen plasma not only increases the hydrophilic property of the ITO surface but also decreases the work function of it, for which we ameliorate the injection of holes. Studies showed that oxygen plasma treatment can decrease the work function of ITO to the order of 10^{-1} while UVOzone can only decrease it to the order of 10^{-2} . However, because PEDOT-PSS is a very strong hole-injecting material, there were no consequential differences

between the two production processes. Sometimes they gave close results for our devices.

2.4 Spincoating.

The advantage of PLEDs over other OLEDs is that PLEDs can be produced by the spin coating technique with a spinner. Some amount of the prepared solution is placed on the substrate and is rotated at a certain speed to obtain a uniform film with a certain thickness. In order to get the desired thickness about the film we usually prepared some blank pieces of glass on which the solution was spin coated with different rotating speeds for each piece. Later, with ET-4000, we measured the thickness of each (or luckily some of them) piece until we got the appropriate thickness under the appropriate rotating speed. Sometimes different substrates would have little effect on the thickness of the solution (for example the thickness of the blend on PEDOT-PSS may be different from that on the blank glass). Fortunately we found the difference was small enough so that we could just ignore it.

In order to get a uniform film, the selection of solvents undoubtedly plays an important role. Experimentally, Xylene, Chlorobenzene, and Toluene are better than THF (tetrahydrofuran), Chloroform (Trichloromethane), and 1,2-dichloromethane. Figure 2.6 showed the AFM films of solutions of THF (upper graph) and Xylene (lower graph). The upper part of the picture showed that a film with THF as the solvent had more holes on the surface and it was also not very uniform. On the contrary, however, films with Xylene as the solvent had more smooth and uniform surfaces. Similar results were discovered in [16].

In order to get a good film, there are some other important factors to which are worth paying attention. For example, we do not drop the solution to the substrate from high altitude. We do not spin coat the solution with the rotating speed lower than one thousand rpm. The last but not least, we always filter the solution before drop casting it with a filter whose aperture is 2 micrometers. In our experiments, we always connected a PE syringe, which is resistive to organic solvents, with the filter. See Figure 2.7.

This gadget promises that the solution passing the filter is clean enough every time when we drop cast the solution.

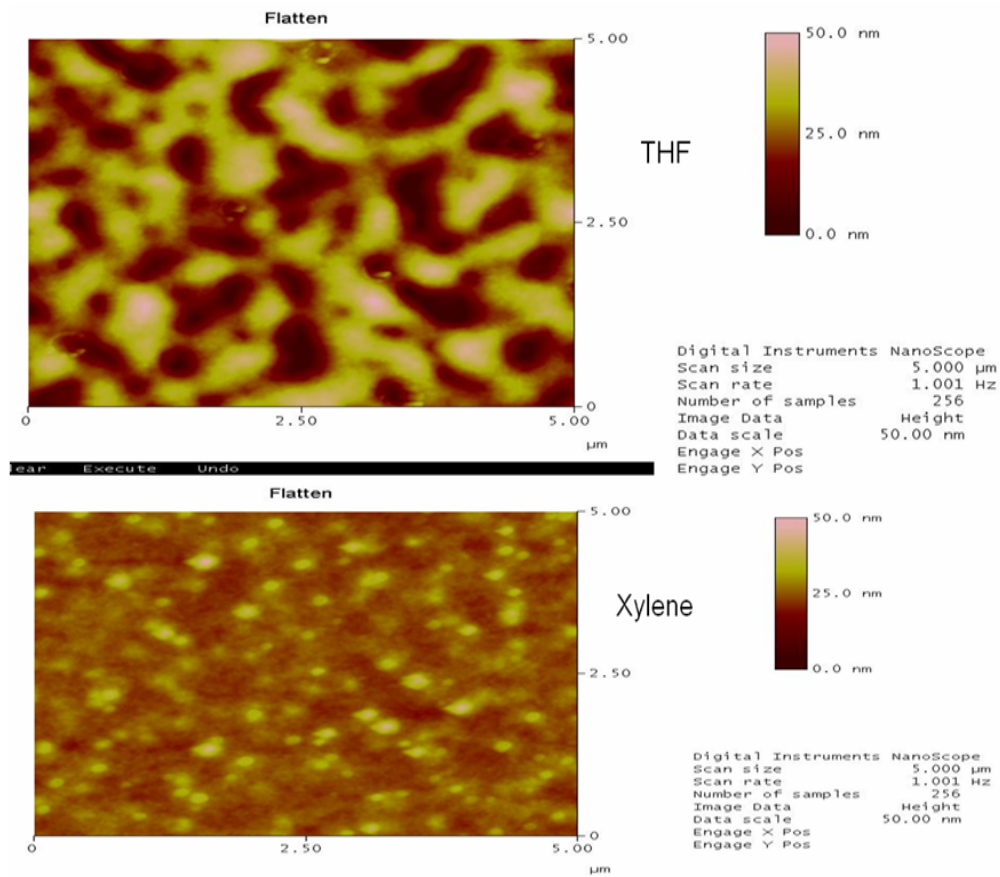


Figure 2.6: Comparisons between films with solvents of THF or xylene. Xylene is a better solvent because solution with it forms uniform and smooth films.



Figure 2.7: The filtering gadget consisting of a PE syringe and a filter.

2.4.1 Spin coating PEDOT-PSS on the ITO.

We usually spin coated the Poly (3, 4 - ethylenedioxythiophene) poly (styrenesulfonate) (PEDOT-PSS) with 2-step rotations. The first one was set to 2,500 rpm for 2 seconds while the second one was set to 6,500 rpm for 30 seconds. Under this circumstance we got a film of 450 Å. Under vacuum, we baked the layer at 100°C for 30 minutes, which was exactly the production condition in the literature. Other people may use 200°C for 1 hour to bake the PEDOT-PSS layer.

2.4.2 Spin casting the first layer on the PEDOT-PSS.

In our case, for single-layer device, which means that the first layer is already the emissive layer, we spin coated it with the rotating speed of 6,000 rpm for 30 seconds. Thus we got thickness of 800 Å. We always baked the layer at 80°C for 30 minutes, which was also suggested in the literature.

For double-layer devices, however, the first layer means the TFB layer. In this case we usually used one per cent TFB that was dissolved in Chlorobenzene. We usually chose the rotating speed so that the thickness of the layer was about 240 Å. This layer usually was baked at 180°C for 40 minutes.

2.4.3 Spin coating the second layer in use of the buffer-layer technique.

The major problem of the solution-processable PLED production is that it is difficult to make multilayer devices. If there is already a polymer film on the substrate that dissolves in an organic solvent, and whenever another amount of organic solvent with the new polymer is cast on the film, the first film will be dissolved as well and be etched away. Therefore, it will not succeed if we spin cast another polymer layer which is dissolved in an organic solvent on the underlying polymer layer which is also dissolved in an organic solvent. Nevertheless, some researches pointed out that we may make use of the hydrophilicity (or hydrophobicity) of a solvent to produce multilayer structures. Gong et al [15] first spin coated the PVK-SO₃Li, which is water dissolvable, as the hole-transporting layer. After this they spin coated the emissive layer which was dissolved in toluene. In this way, the emissive layer would not etch the underlying hole-transporting layer, which was ethanol soluble. Finally they spin cast the t-Bu-PBD-SO₃Na, which was also dissolved in ethanol, as the electron-transporting layer. Owing to the same reason of the survival of the first water-soluble layer when the second emissive layer was done, the third layer did not etch the second layer, either. One can easily figure out that the method only focuses on several special

conditions of polymers. Under most cases, we need to synthesize water-soluble organic compounds as they did. This delimits the application of the method to different kinds of solutions.

We develop a method that can probably be applied to a majority of production conditions. First we notice that we have to prevent the first polymer layer from being etched when we make the successive layer. It is imperative that there is no contact between a soluble polymer film and an organic solvent when spin coating a new polymer layer. By doing so, we introduce a kind of liquid material. The material must not interact with all the organic solutions we use. Secondly the material must be removable by baking after the second layer is done. Fortunately we find the colorless sticky liquid, 1,2-propanediol (glycol), perfectly suits our need down to the ground. In addition to inactive to our organic layers and removable by baking at a certain temperature after spin coating the subsequent polymer layer, the viscous characteristic of the material under low temperature improves the yield on producing bi-layer structures.

The overall fabrication process of a typical bi-layer structure consists of the following steps. Assume that we have already done the first organic polymer layer and we also have baked the layer, annealing it as well. We fetch some glycol from the refrigerator whose temperature is usually lower than 4°C. To begin with, we put some amount of glycol on the sample containing the first layer, shown in Figure 2.8.

Since we just need a thin glycol layer to protect the first layer, we spin coat the pure glycol chunk to spread it around the surface of the substrate. Extravagant amount of glycol would possibly make a bad second layer. The next step is tricky. After we spin coat the glycol layer for a while (usually less than 1 second), we stop rotating, leaving a thin layer of it. The thin glycol layer will contract (at least for the underlying layer being TFB or PFO. However, it will not contract on the LEP surface). Figure 2.9 shows the contracting thin glycol layer.

When the thin glycol is contracting and the spinner stops rotating, we drop cast the second layer (for example drop casting the LEP layer) as quickly as possible. Afterwards, we start rotation again before the thin glycol layer contracts to the area which is smaller than the one we drop cast our solution. If the glycol layer contracts back to an area which is smaller than the one on which the solution is drop cast, the underlying layer will definitely be etched by the second layer, resulting in failure of our device. Figure 2.10 shows the way we drop cast the solution on the thin, contracting glycol layer and Figure 2.11 shows the regeneration of the spinning after all the processes are done.



Figure 2.8: Applying some amount of glycol on the TFB layer.

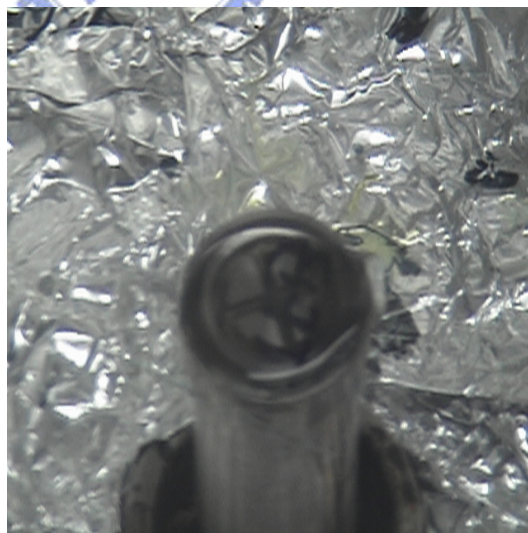


Figure 2.9: Spincoating for a while after the glycol is applied. The majority of the glycol will be spincoated out, leaving a contracting thin layer.