

# III

## Fabrication of the samples

The fabrication of the samples for SPR measurement consists of three steps. It begins with glass substrates cleaning using ultrasonication, followed by the deposition of a metal thin layer by electron beam gun apparatus. The process is completed with the thermal evaporation of an organic thin film using resistively heated sources.

### III.1 Glass substrate cleaning

Clean glass substrates are important to assure the good planarity of the thin film deposited, a parameter that affects the determination of the thickness and dielectric function of the different layers of the sample. In ultrasonic cleaning, the substrates are agitated at ultrasonic frequencies in order to move out contamination via cavitation. Ultrasonic cleaning is most effective on particles larger than 3-5 microns. The cleaning procedure we used for glass substrates consists in the following steps:

1. The substrates are put in a solution of neutral detergent and deionized water. The solution is heated for 15 minutes at  $90\text{ }^{\circ}\text{C}$ , subsequently the substrates are rinsed with normal water.
2. The substrates are vertically suspended in deionized water and washed in ultrasound for 15 minutes. This process is repeated once.
3. The substrate are put in acetone and washed in ultrasound for 15 minutes.
4. The Substrates are put in isopropyl alcohol and washed in ultrasound for 15 minutes.
5. The substrate are vertically suspended in deionized water and washed in ultrasound 15 minutes.
6. Finally, substrates are placed on the stove at  $100\text{ }^{\circ}\text{C}$  for 12 hours.

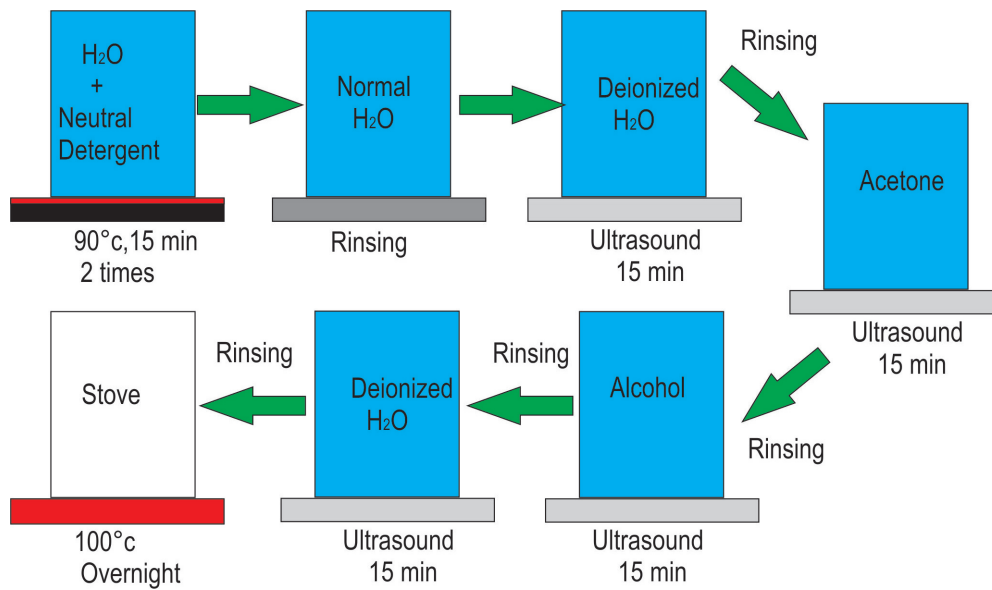


Figure III.1: Glass substrate cleaning.

## III.2 Vacuum deposition

Vacuum deposition is a physical vapor deposition (PVD) in which the atoms from a thermal vaporization source reach the substrate without collisions with residual gas molecules in the deposition chamber. It requires a vacuum of better than  $10^{-4}$  Torr in order to have a long mean free path between collisions. High vacuum environment ( $10^{-7}$  Torr) may be used to produce a film with the desired purity, depending on the deposition rate, reactivities of the residual gases and depositing species [Bishop11].

Thermal vaporization requires that the surface and generally a large volume of material is heated to a temperature at which there is an appreciable vapor pressure. Common heating techniques for evaporation/sublimation include resistive heating, electron beam (e-Beam), gun assisted heating, and inductive (rf) heating. Resistive heating is the most common technique to vaporize material at temperatures below about  $1500^\circ C$ , while focused e-Beams are most commonly used for temperatures above  $1500^\circ C$  [Mattox10].

### (a) E-Beam gun assisted deposition

In this technique electrons are generated by a thermionic source, a tungsten filament heated by an external current. Electrons are accelerated by high voltages thus obtaining an electron beam. Electrons are directed and focused to hit the source material using a magnetic field.

Metals were deposited by an e-Beam gun apparatus (model Univex 450) in high vacuum ( $10^{-6}$  Torr) environment, in the clean room of the Laboratório

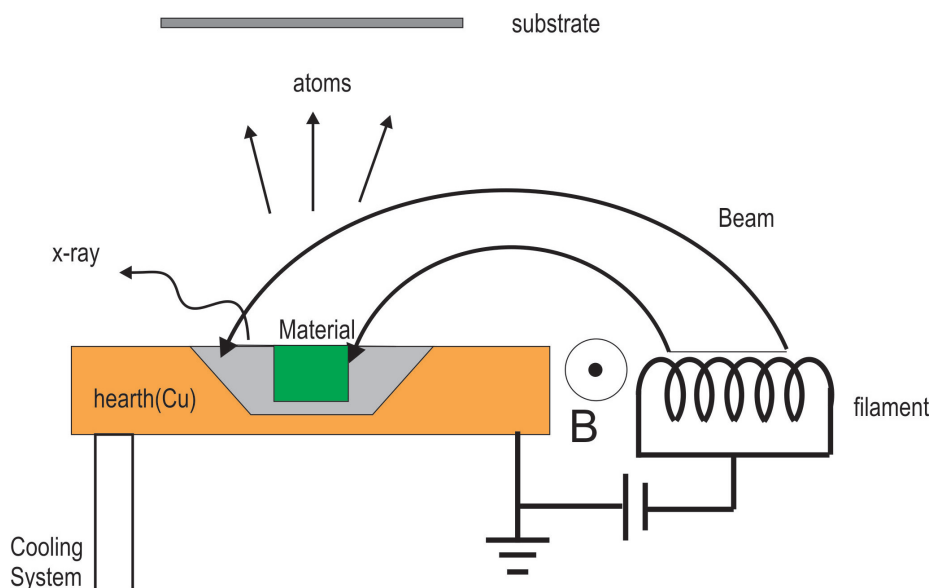


Figure III.2: Scheme of the e-beam gun system.

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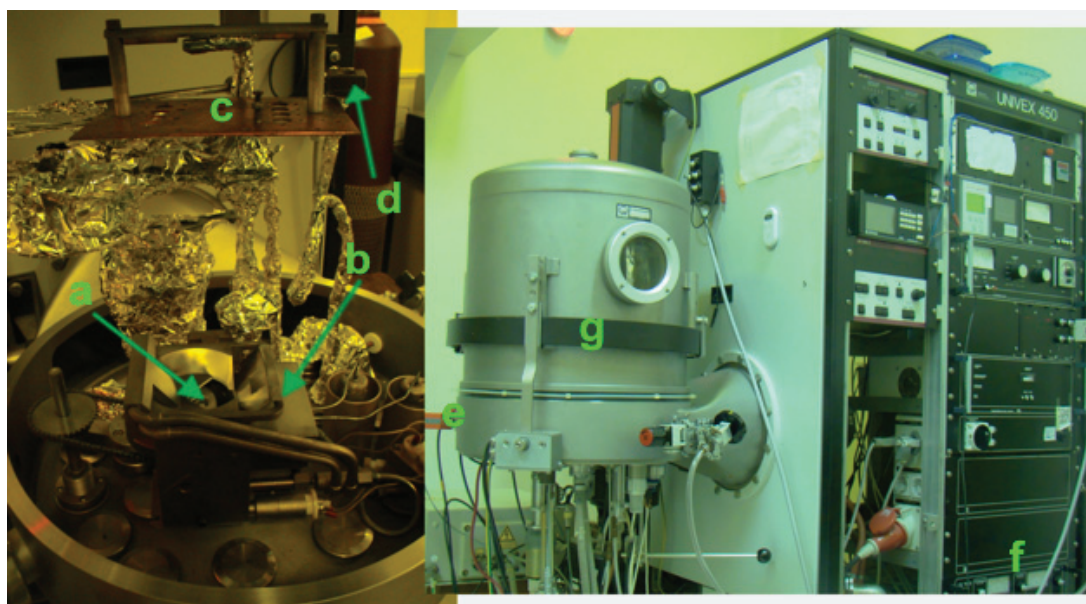


Figure III.3: Univex 450. a- crucible with metal pellet, b- tungsten filament, c- sample holder, d- quartz crystal balance, e- pressure detector, f- electron gun controller, g- vacuum chamber.

The vacuum is made by a mechanical pump in series with a turbo molecular pump able to reach a pressure of  $10^{-7}$  Torr. For the pressure measurement the system has two sensors: a Pirani type for low vacuum, and Penning type for high vacuum. The e-Beam gun system has a rotating stage with multiple crucibles. The rotating stage was designed in the laboratory and it's made of

copper. The crucibles, of FABMATE material (99.9995% elemental carbon) were purchased from Kurt J. Lesker Company.

The interior of vacuum chamber has a quartz crystal microbalance with a resolution of 0.01Å, used to measure the thickness of the deposited layer. Because of the rate at which the material is deposited on the sensor may be different from the one at which it is deposited on the glass substrate, a correction factor, commonly named as tooling factor (TF), is introduced manually in the control panel of the thickness monitor system. The correct value of the TF is defined as

$$TF(\%) = TF_i \left( \frac{t_A}{t_Q} \right), \quad (1)$$

where  $TF_i$  is the initial random tooling factor,  $t_A$  is the actual thickness of the deposit on the substrates and  $t_Q$  is the thickness read by the quartz balance. To establish the tooling factor relative to the depositions, we started introducing on the control panel an arbitrary value of the TF equal to 100. The Actual thickness of the deposition is then measured using a profilometer, and the correct value of the parameter TF is obtained using equation (1). This value of the TF is then used to perform calibrated depositions, and is introduced manually on the control panel together with the density and Z-Factor characteristic of the material deposited.

The univex 450 controller allows the automated control of the deposition with the setting of the desired deposition rate, final thickness and maximum current of the electron beam. Nevertheless, the intensity of the current can be programmed to follow a desired behavior. Figure III.4 shows the typical intensity curve which can be set from the control panel. At time  $t=0$  there is no power supplied to the filament. During “rise time 1” (RT1), power is gradually increasing up to “soak power 1” (SP1), and held during “soak time 1” (ST1) to allow the degassing of the metal pellet.

During the “rise time 2” (RT2) power increases to “soak power 2” (SP2) and is maintained over “soak time 2” (ST2). Often, at this stage, is reached a deposition rate that is below the desired value. After, the controller starts increasing again the power until the desired deposition rate is established. The power never exceeds the maximum value set on the control panel.

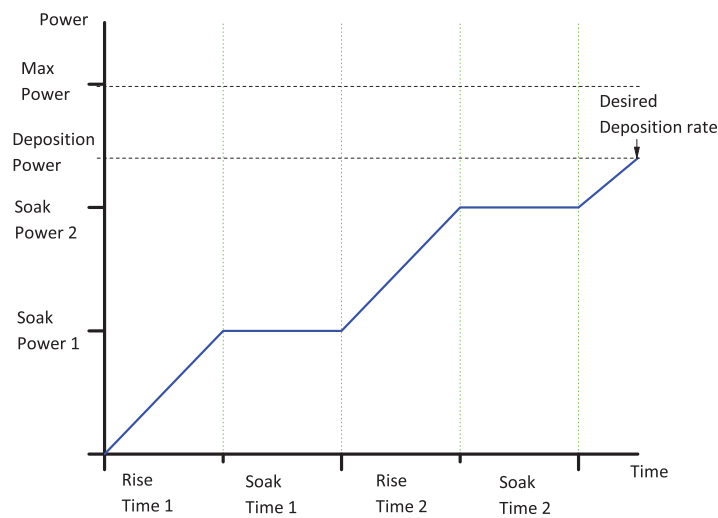


Figure III.4: Power Curve for Univex 450.

The following is a table of the parameters that fully characterize the gold and silver depositions.

							Power	
Metal	RT1	SP1	ST1	RT2	SP2	ST2	Max.	deposition
Au	60 s	3 %	60 s	60 s	6 %	60 s	10%	7%
Ag	60 s	8 %	60 s	60 s	16%	60 s	26%	22%
	$\rho$ ( $g/cm^3$ )	P (Torr)		TF %	Z-ratio	rate ( $\text{\AA}/s$ )		
Au	19.30	$2.5 \times 10^{-6}$		200	0.381	1.9		
Ag	10.59	$2.2 \times 10^{-6}$		173	0.529	2.1		

Table III.1: Experimental parameters that characterize the gold and silver depositions.

These parameters may change because of filament degradation with time. For this reason is better to replace tungsten filament after some depositions. [Gevlber04].

### (b) Thermal evaporation

This technique of evaporation was used to deposit the thin luminescent organic film to be analyzed, and consists in the heating of crucible containing the material to be deposited by Joule's effect. The crucible is generally a boat or a baffle source made of Tungsten, Carbon or Molybdenum.

Low DC voltages and high currents are applied to metal electrodes connected to the crucible and current is slowly increased to avoid mechanical stresses until sublimation or evaporation of the material is reached [Mattox10].

Thermal evaporation was performed using an apparatus model Univex 300 in the clean room of the LOEM Laboratory at PUC-Rio. The whole system is very similar to the one used to perform metal depositions, with vacuum pumps, pressure sensor and a quartz crystal balance to control the thickness of the deposition.

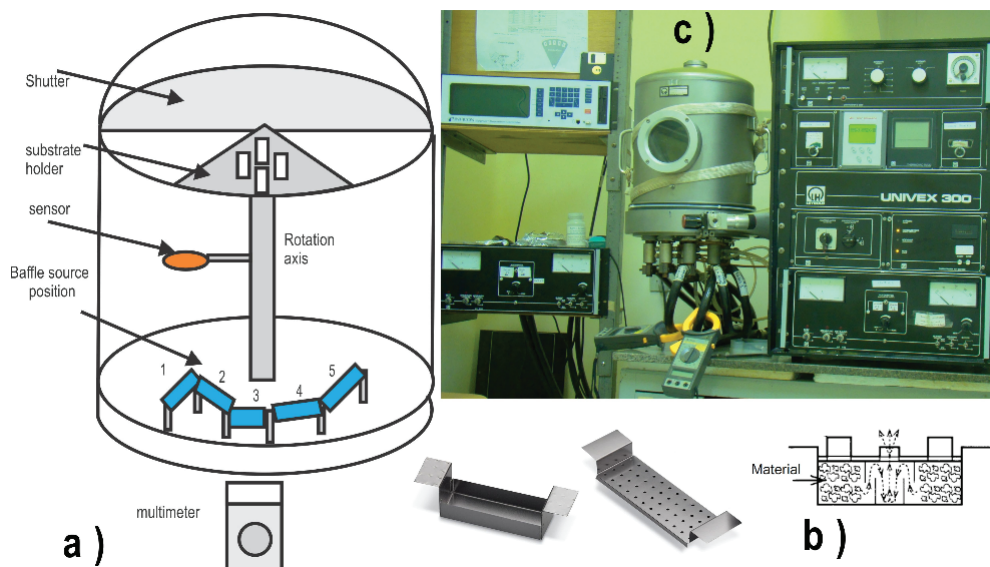


Figure III.5: a) schematic diagram of the vacuum chamber Univex 300. b) baffle source c) photo of the thermal evaporator Univex 300.

The vacuum system achieves pressures of about  $10^{-5}$  Torr. The current to heat the boat is supplied by two stabilized voltage sources Model 300Tr-1A, and is measured with a multimeter model Minipa ET3200A.

We used this apparatus to deposit  $Alq_3$  [Dalansinki04], a commercial organic luminescent material purchased from Luminescence Technology Corp. (LumTec) with a purity of 99%. The next table list the parameters that characterize the deposition of  $Alq_3$ .

	$\rho(g/cm^3)$	P (Torr)	TF %	Z-ratio	rate ( $\text{\AA}/s$ )	I (A)
$Alq_3$	1.45	$1.4 \times 10^{-5}$	58.2	1	1.2	18

Table III.2: Experimental parameters that characterize the  $Alq_3$  thermal evaporation.

To measure the TF relative to the metals and the organic material, a deposition of 100 nm of each material was made on Silica substrates. The thickness of the deposition was measured using a profilometer of VEECO, model Dektak150,

with a resolution of  $\pm 5$  nm. The profilometer uses a diamond stylus ( $Radius = 12.5\mu m$ ) to perform a step height measurement. The height position of the diamond stylus generates an analog signal, which is converted into a digital signal stored, analyzed and displayed on the computer. The stylus force was 2-3 mg for metal and 1 mg for dielectric sample ( $Alq_3$ ). The scan length was 400-800  $\mu m$ , with scan time of 30 s.

Each measurement was performed on different parts of the sample to account for the possible non homogeneity of the deposition. The final relative uncertainty of the measured TF was 10%. With this procedure we can assure that the actual thickness of the depositions is the one read by the quartz crystal balance with an uncertainty of 10%. The next figure represents the measurement of the 100nm thin film of  $Alq_3$  with the profilometer, before setting the actual tooling factor.

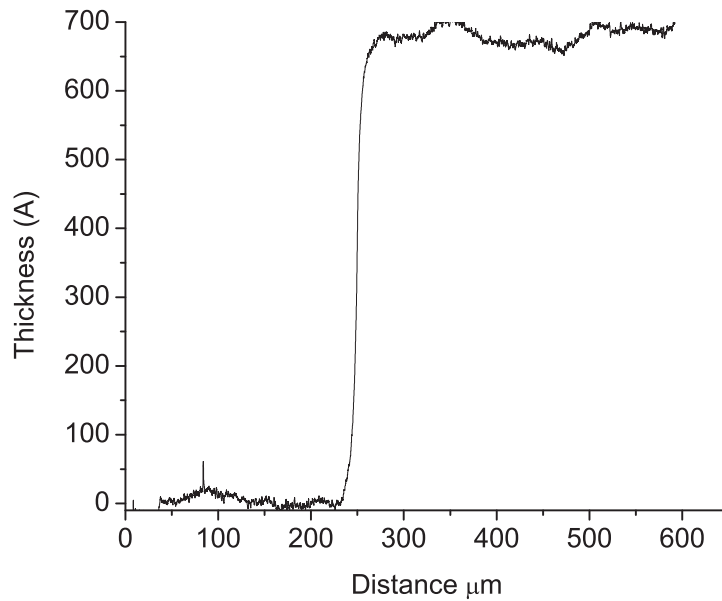


Figure III.6: Height profile obtained using the profilometer for a deposition of 1000Å (nominal thickness) of  $Alq_3$ .



### III.3 Final samples

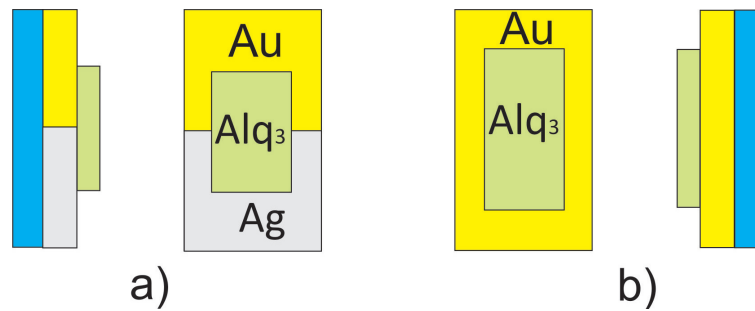


Figure III.7: Structures of the samples used to measure the refractive index of  $Alq_3$  (a) and to monitor its degradation (b). In blue glass slide.

Figure III.7 shows the final structure of the different samples that were analyzed by SPR spectroscopy. The structure a) was used to measure the thickness and refractive index of the thin organic film with a unique deposition of  $Alq_3$  over different metal depositions on the same glass substrate (Ag and Au). The structure b) was used to monitor the deposition of  $Alq_3$  over a gold film when exposed to atmosphere. It is well known that  $Alq_3$ , a common electronic transporting material used in the fabrication of OLED, is extremely reactive to light and atmospheric exposure [Rosselli09, Kolosov01, Popovic02, Schaer01]. For this reason, the samples used to measure the dielectric constant of the thin organic film were kept in a dark environment and encapsulated using a simple process sketched in figure III.8.

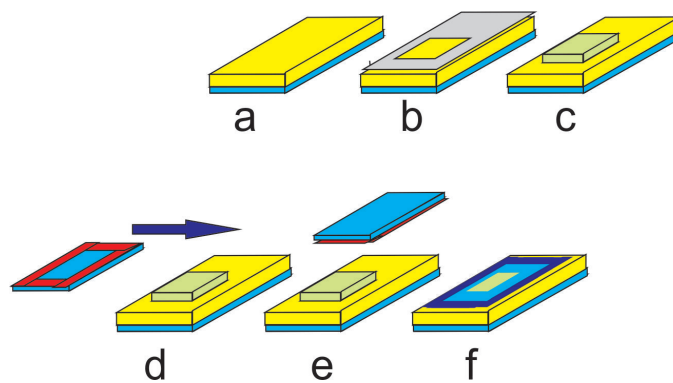


Figure III.8: Procedure to encapsulate the samples. a- gold film, b- mask on gold film. c- deposition of dielectric material, d- glass slide with tape. e- glass slide with tape put over the sample. f- epoxy adhesive on sample.

First, we put a clean glass slide with a lower area on gold/ $Alq_3$  film (step d in figure III.8). On the edge of the glass slide is attached double-sided bonding tape (d-e). Once the glass slide has been attached to the gold film, the contour is coated with an epoxy adhesive (araldite hobby 10 min) (f). Finally, the



sample is left in a glove box for 2 hours. Figure III.9 shows a photo of one of the encapsulated samples.

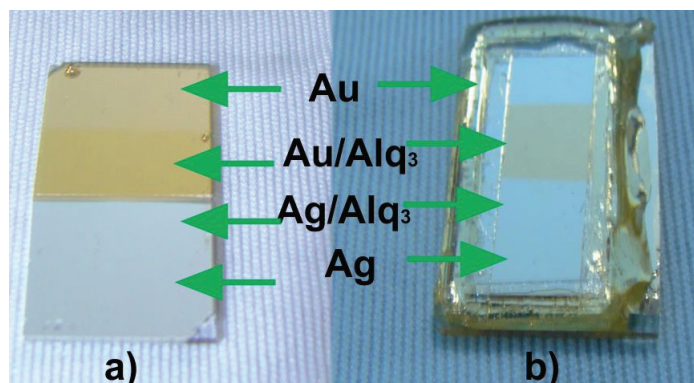


Figure III.9: Photo of a non encapsulated sample (a), and a encapsulated sample (b).