VI
Conclusions

It was assembled an automated Surface Plasmon Resonance spectrometer with an angular resolution of about 0.0025°. The SPR spectrometer allows the study of samples in a dark environment and is equipped with large area Silicon home-made detectors (1 cm× 2 cm) that assure the possibility to measure the curve of reflectivity in a wide angular range of about 20°. The experimental set-up has been automated by an home-made acquisition data software developed in *LabView* platform, and the data were analyzed using the free software *Winspall* 3.02, which performs an iterative fitting procedure on the experimental data in order to obtain the values of the thickness and refractive index of each one of the planar layers constituting the sample under analysis. The spectrometer was first evaluated on the characterization of gold and silver thin films, fabricated by e-Beam gun assisted deposition in the clean room of the Laboratório de Espectroscopia Óptica e Optoeletrônica Molecular (LOEM) at the Department of Physics in PUC-Rio. The dielectric constants of the metal thin film were measured at a wavelength of 632.8 nm and the values obtained are in good agreement with the ones found in literature [Simon75, Bruijn91]. The non homogeneity of the metal depositions has been taken in account measuring the thickness and the complex dielectric constants in about 10 different regions of the samples. The uncertainty in the measurement of these parameters has been calculated as the standard deviation obtained from the dispersion of the experimental data relative to the different zones of the sample. This statistical approach together with the possibility to acquire the SPR curve in a wide angular range, led to the determination of the thickness and real part of the dielectric constant with an accuracy better than 0.6%. Using a novel Two-Metal Substrate Technique on encapsulated samples we was able to perform the simultaneous measurement of the thickness and index of refraction of a thin organic film ($\approx$ 22 nm thick) of Alq_3, deposited via thermal evaporation on thin silver and gold films. To our knowledge, this is the first experimental demonstration of the Two-Metal Substrate Technique, up to now only theorized in literature [Bruijn91]. We measured the real part of the index of refraction of the organic thin film at a wavelength of 632.8

nm with an accuracy of 4%, obtaining a value of 1.74[1.68;1.83], in good agreement with the values found in literature using ellipsometric techniques [Kumar05, ElNahass10, Celii97, Muhammad11, Djusiric02, Dalansinski04]. The accuracy of the measurement of the refractive index of organic materials by ellipsometric techniques is usually about 0.5% [Kostruba97], with the further advantage to access its complex part and its dispersion with wavelength [Pascu12]. The most important drawbacks of these techniques are the necessity of very complicated optical models for the data analysis and a quite higher cost in comparison to a standard SPR spectrometer. Nevertheless, the accuracy of the SPR based measurements could be enhanced by the use of a temperature stabilizer on the glass slides during the thin film deposition process and on the sample holder during the SPR spectroscopy analysis. Further improvement would be given by the use of a lock-in based optical detection in our apparatus. In this context, a hypothetical accuracy of 0.3% in the determination of the optical constants of the metal supporting the plasma wave, would lead to an uncertainty of 2% in the determination of the real part of the refractive index of organic materials.

In the last part of the thesis we studied the degradation process of a non encapsulated sample by SPR spectroscopy in dark environment. The non encapsulated sample, composed by a thin Alq_3 film deposited over a thin layer of gold, has been monitored continuously for about 48 hours. The results show a progressive decrease of the value of the angle of resonance of the system with atmospheric exposure, coherent with the results reported in [Djusiric02]. Here a 3% decrease of the value of the real part of the refractive index of a thin film of Alq_3 on glass slides was observed by ellipsometric technique after 72 hours of atmospheric exposure, probably due to the known crystallization process of the Alq_3 when exposed to humid atmosphere [Popovic02, Hassan07]. Our study reveals a further modification: during the 2 days of monitoring, the FWHM and the minimum value of the SPR curve present a progressive increase, which can be attributed to the degradation of the $gold/Alq_3$ interface. XPS measurements on a $gold/Alq_3$ interface in vacuum excludes the possibility of chemical interaction between gold and Alq_3 [Turak02], but no study has been performed up to now on samples kept in atmospheric environment for some days. The broadening of the SPR curve might be explained considering a progressive corrugation of the metal-dielectric interface with the creation of a very thin effective intermediate layer between the gold and the organic deposition. This layer could be modeled using the so called Maxwell-Garnett theory [Pan09, Kanso07] which, in our case, would predict a negative shift of the angle of resonance together with a progressive increase of the FWHM and minimum value of the SPR curve. Another possible explication comes from the formation of the so called dark spots in OLEDs [Hassan07]. From literature is known that the degradation of Alq_3 is due to two independent processes: an intrinsic process and an extrinsic process [Hassan07]. The first one is related to electrical stress and leads to the loss of electroluminescence efficiency. The second one is related to the formation and growth of non-emissive areas known as dark spots [Hassan07]. There are various mechanisms proposed to explain the formation and growth of dark spots: molecules of water vapor from the air can diffuse into the material through the microscopic pinholes and grain boundaries formed during the deposition of the organic material [Schaer01]. Dust particles from the surroundings can also deposit during and after the deposition and create large defect sites that emerge as dark spots [Kolosov01]. In this sense, the broadening of the SPR curve of the Alq_3/gold sample could be associated to the presence of defect sites growing with time and acting as efficient scattering elements of the surface plasmon polariton propagating along the metal-dielectric interface. In order to clarify the origin of the deformation of the SPR curve, in the future are programmed new observations of the degradation process of the metal organic interface, AFM measurements on the Alq_3 surface and Surface Enhanced Raman Spectroscopy (SERS) measurements on fresh and air exposed $gold/Alq_3$ interfaces.