

I

Introduction

Surface Plasmon resonance (SPR) was first observed by Wood in 1902 [Wood02]. He was not able to explain the anomalous intensity drops in the intensity of light that was reflected from an optical metal grating at certain precise angles. In 1941 Fano [Fano41] explained the relation between Rayleigh's theory and observations by Wood considering a surface electromagnetic wave mode propagating along the metal dielectric interface and introducing the concept of polariton, that is, a quasi-particle resulting from the coupling between the electromagnetic waves and the collective oscillation of electrons. In 1952 Ritchie [Rit52] observed the diffraction of electron beams by thin metal films. He predicted that fast moving charged particles could excite surface waves in metals, and considered such modes as elementary excitations in solids. Optical excitation of surface plasmons with visible light by the method of attenuated total reflection (ATR)[Zhu86] was demonstrated by Otto [Otto68] and Kretschmann and Raether [Kret68] independently in 1968. In the decades of 70' and 80', Surface Plasmon Resonance (SPR) spectroscopy has been successfully applied to the interrogation of thin films and used to develop Chemo/Bio sensors with high selectivity and sensitivity, observing molecular interactions without the need to label the interacting species. In 1976 Abeles [Abeles76] applied for the first time SPR spectroscopy to study the optical properties of thin films, in 1982 Liedberg demonstrated the first SPR bio-sensor prototype [Liedberg82, Damos05, Bruijn91] and in 1990 was developed the first commercial SPR based bio-sensor by Biacore [Ligler95]. In the last years SPR spectroscopy has been applied to a variety of applications, from liquid refractive index measurements [Mehan05] to real-time monitoring of noble metal surface functionalization [Liang10], gas detection and immune-sensing [Liedberg82] [Mitchell10].

The major limit of SPR spectroscopy in the monitoring of physical or chemical processes occurring at a metal-dielectric interface is the impossibility to determine simultaneously with a unique measurement the thickness and the refractive index of the thin molecular organic films deposited over the metal supporting the plasma wave.

Two common experimental procedures for the simultaneous determination of thickness (d) and refractive index (n) are named as Two-Colors or Two-Medium methods, and were demonstrated experimentally for the first time in 1991 by Bruijn [Bruijn91]. These methods consist in performing two independent measurements over the same sample changing respectively or the wavelength of the exciting electromagnetic radiation or the refractive index of the external fluid (i.e. air, water, water-glycerin solution). Each of the two measurements gives a continue set of couple of values (n, d), and the intersection point of these curves correspond to the actual values of the parameters. Unfortunately, these procedures can be applied only if the dispersion function of the organic film is known or if the external fluid in contact with the thin organic film does not produce any alteration on the physical or chemical properties of the organic species [Bruijn91, Peter96]. While thin organic films deposited with self-assembling technique in liquid environment do not suffer this limitation, it is well known that most of thermally evaporated organic luminescent thin films are extremely reactive to liquid and atmospheric environment [Schaer01, Rosselli09]. For this reason, luminescent organic thin film properties are generally investigated by ellipsometric technique in vacuum environment [Djurisic03], and to our knowledge there is no mention in literature about the simultaneous determination of their dielectric function and thickness by SPR spectroscopy. In the work of this dissertation we demonstrate that a careful process of fabrication of planar multilayer metal-organic samples, followed by a simple encapsulation procedure, allows the simultaneous determination of the parameters of the luminescent organic film using a double-metal substrate, covered half with silver and half with gold depositions. We tested this method on the thermal deposition of a thin film of Alq_3 , a typical luminescent organic molecule with a well known refractive index [Dalansinkki04, Zawadka14], at today widely used in the fabrication of organic light emitting diodes (OLEDs) [Jung06]. Moreover, we monitored in real-time by SPR spectroscopy the process of degradation of the Alq_3 /gold interface when exposed to atmosphere, observing a shift in the angle of surface plasmon resonance proportional to the observation time, consistent with a possible change in the value of the refractive index of the organic thin film.

In the first chapter of the dissertation we describe the electromagnetic theory of SPR spectroscopy and the basic concepts of SPR sensing. The second and third chapters describe the process of fabrication of the planar multilayer metal-dielectric samples and the characteristics of our home-assembled SPR spectrometer. In the fourth and last chapter we present the experimental results on the characterization of the optical constants of the metal and organic

thin films in terms of absolute value and homogeneity, together with the monitoring of the degradation process of the Alq_3 /gold interface.