Sub-Monolayer Sensitivity in VUV Ellipsometry Investigations of Organic Thin Films

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Vacuum Ultraviolet (VUV) Spectroscopic Ellipsometry (SE) measurements were performed *in situ* for the optical characterization of ultra-thin organic films on H-passivated Si(111).

With the reduced size of future devices the effects of dimensionality are becoming more and more important. Ellipsometry is a non-destructive and very sensitive surface and thin film measurement technique which can detect the changes in the optical response produced by an overlayer on a smooth surface. However, interpreting the ellipsometry spectra for very low coverages (below few nanometers) down to a monolayer or even submonolayer regime remains a challenging task as the optical path of the light through the material is much smaller than the wavelength [1]. In this case the light has a reduced sensitivity to the refractive index of the film which is strongly correlated with the film thickness. Consequently only the product of these parameters can be uniquely determined [1].

The smaller wavelength of the UV light accessible at BESSY is more sensitive to low coverages. The organic materials used in the investigations are *tris*-(8-hydroxyquinoline)-aluminum(III) (Alq$_3$) and N,N'–Di-[(1-naphthyl)-N,N'-diphenyl]-(1,1'-biphenyl)-4,4'-diamine (NPD) (fig 1). These materials are among the most commonly used as electron-transport (Alq$_3$) and hole-transport (α-NPD) materials in light emitting applications OLEDs [2-6].
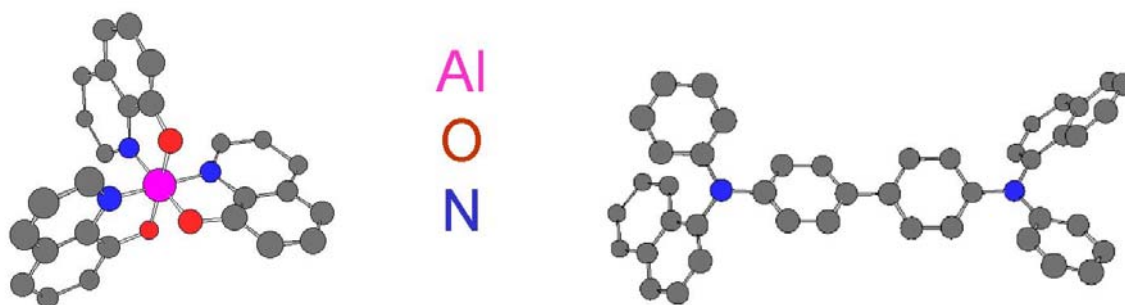

Figure 1. Molecular structures of Alq$_3$ and α-NPD

As can be seen in fig. 2 the changes in the optical response induced by the overlayer when compared to the H-Si(111) substrate are significant even for very low coverage. In the inset the thicknesses calculated from a quartz microbalance calibration are compared with the ones from the ellipsometry evaluation. The "ellipsometry" thicknesses are in very good agreement with those calculated from the frequency shifts indicating that ellipsometry is also an excellent tool for thickness monitoring.
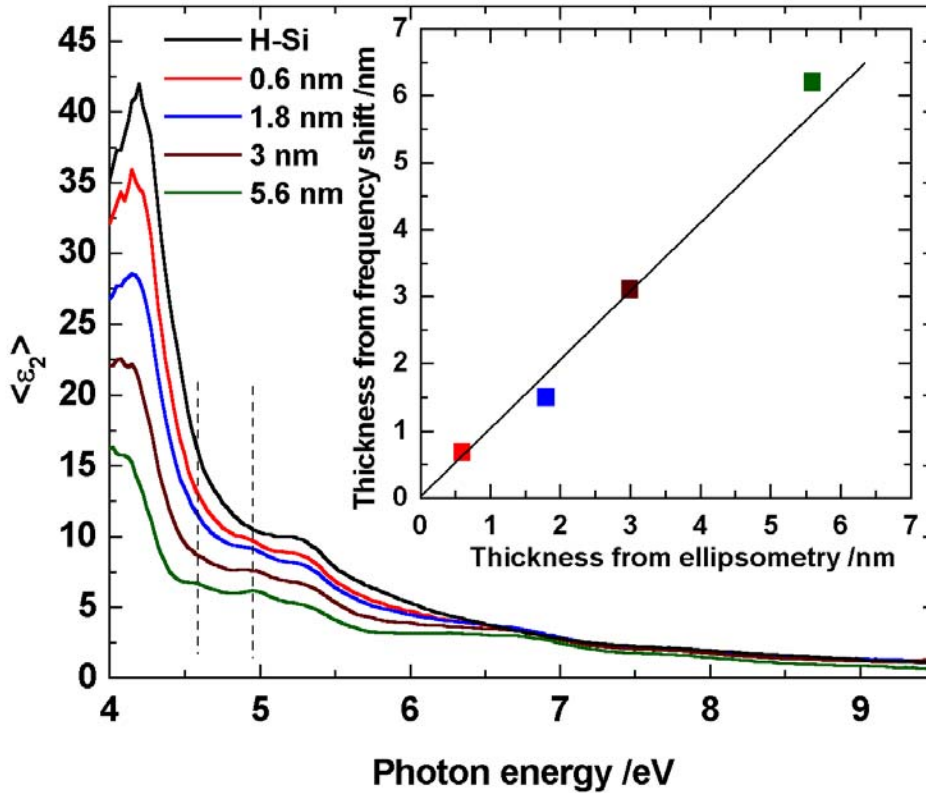
Figure 2. The effective $\langle\varepsilon_2\rangle$ of the Alq$_3$ samples compared with the $\langle\varepsilon_2\rangle$ of the H-Si(111) substrate. Vertical dashed lines mark the positions of strong Alq$_3$ induced features.

The strong changes in the experimental spectra indicate that for strongly absorbing organic materials a numerical fit for the optical constants can be performed even for very low coverages. Figure 3 shows for comparison the imaginary part of the dielectric function ε_2 of bulk Alq$_3$ compared with the one of a submonolayer deduced from a three phase model [1] substrate\film\ambient.
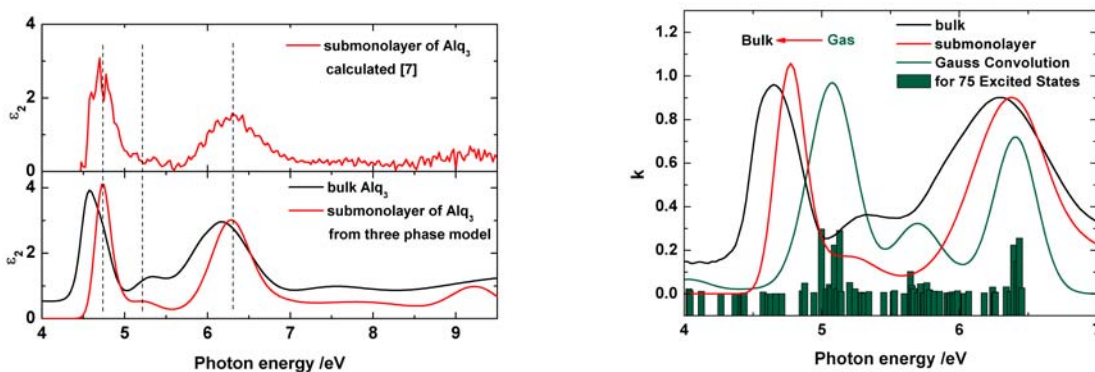

Figure 3. Left - comparison between the imaginary part of the dielectric function for a submonolayer of Alq$_3$ obtained from a three phase model and calculated [7]. The imaginary part of the dielectric function for bulk Alq$_3$ is also plotted.
Right – Comparison with theoretical calculation for 75 excited states.

The validity of the solution was checked using a direct calculation method [7]. In this case the calculated ε_2 is affected by the experimental noise of two different measurements, namely that of the H-Si(111) substrate and of the ultra-thin Alq$_3$.

The dominant features of the dielectric function in fig. 3 were assigned by comparison with the singlet-singlet transitions calculated using the Gaussian 98 software [8]. The molecular geometry of the *meridional*-isomer [9] was optimised using the Kohn-Sham density functional theory (DFT) with the 3-21G basis set and the Becke three-parameter hybrid exchange correlation functional (B3LYP). The time-dependent density functional theory (TD-DFT) was subsequently employed to calculate the excitation energies, oscillator strengths, and excited-state compositions in terms of excitations between occupied and unoccupied orbitals.

The differences between the calculated spectra for single molecule, submonolayers and bulk can be explained by a change in either electronic coupling or due to a molecular ordering of the Alq$_3$ molecules in the bulk.

A similar blue shift was obtained for ultra-thin NPD films. Further investigation are necessary in order to see how is correlated the amplitude of the shift the film thickness. This will provide valuable information not only about the electronic transitions in ultra-thin films, but also about the growth mode of the organic layers.
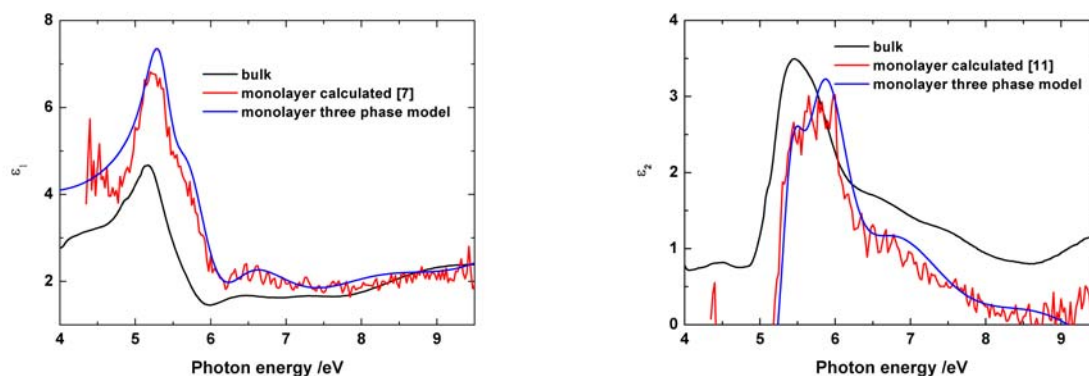
Figure 4. Comparison between the dielectric functions of the bulk NPD and monolayer. Left – real part. Right – imaginary part.

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