HORIBA
Scientific

Application Note

Chemistry

Spectroscopic Ellipsometry

SE28

Characterization of Ultra Thin Surfactant Films by Spectroscopic Ellipsometry

Measuring film thickness at the nano-scale remains a challenging application for spectroscopic ellipsometry for two main reasons. Firstly the reliability of the extracted film parameters depends on the sensitivity of the ellipsometric data in picking up both film thickness and optical constants information. Since the ellipsometric data are collected close to the detection limit, any error inherent in the data will be passed to the predicted film thickness and optical constants. Secondly, a strong correlation exists between film thickness and optical constants when measuring ultrathin layers.

As a consequence, in most of ultrathin film ellipsometric data analysis, the calculation of the film thickness is done by using predetermined values for the refractive index. The thickness is calculated from the assumption that the film is homogeneous and the refractive index is kept constant and estimated either from the literature or measured using another technique (e.g. Abbe refractometer). As the film thickness and the refractive index are strongly correlated, the choice of the refractive index has a strong influence on the value obtained for the film thickness and may cause inaccuracy in the calculated value for thickness.

This application note deals with the characterization of ultra thin surfactant films by spectroscopic ellipsometry. It especially demonstrates the excellent sensitivity of the UVISEL Phase Modulated Spectroscopic Ellipsometer, making possible the decorrelation of thickness and optical constants in an evaluated range of thickness.

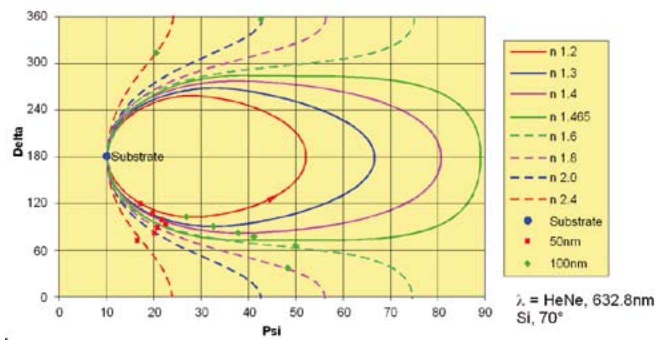
Introduction

Non-ionic surfactants find widespread industrial application in detergency, dispersion stabilization, foaming and emulsification. They are also commonly used as stabilizers of thin films including wetting films. Therefore, the equilibrium and dynamic adsorption of surfactants at the air-water and solid-water interfaces are critical information. A common method of studying surfactant adsorption at the air-water and solid-water surfaces is to use a pressure balance technique and interpret the surface tension as a function of bulk concentration. However, this method is rather imprecise since even small errors in the tension values may cause large errors in the derived surface excess concentrations. Additionally, the restricted amount of information provided by such a technique limits the understanding of the adsorption process. **Spectroscopic ellipsometry is a powerful technique for thin layer characterization and has the required sensitivity for thin films at the nanoscale**.
Furthermore ellipsometry is not limited to information related to the amount of adsorbed surfactant. Process knowledge can be gained by determining both thickness and optical constants of the film.

Determining the sensitivity of the HORIBA Scientific UVISEL Ellipsometer for a 3nm thick layer

Basics: Delta/Psi trajectories for single layers on a subtrate

The simulations below shows the Psi-Delta curves for a simple layer on a silicon substrate, with various refractive indices, at the wavelength λ=632.8nm.



Obviously the Psi-Delta curves converge at the substrate point with nearly the same slope. This means that the thinner the layer is, the higher the sensitivity of the ellipsometer must be to resolve the curves of the different refractive indices values.

Methodology for determining the resolution of the UVISEL providing thickness + refractive index independently

Simulations of Psi-Delta curves were performed for the following sample: top layer / SiO_2 (30nm) / Si substrate. The different simulations correspond to the following refractive indices of the top layer n=1.456, n=1.460, n=1.498, n=1.514, n=1.535 and n=1.572. The points on the curves indicate thickness values of the top layer from 0 to 5nm with 1nm step.

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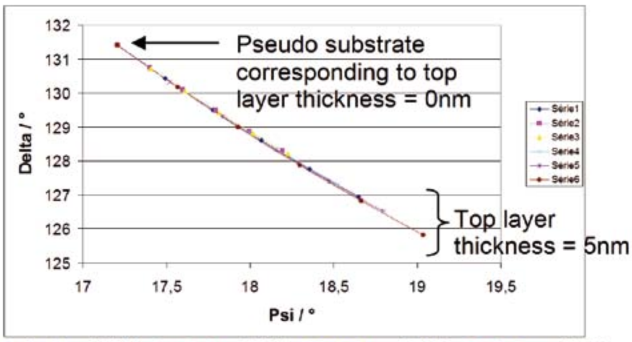
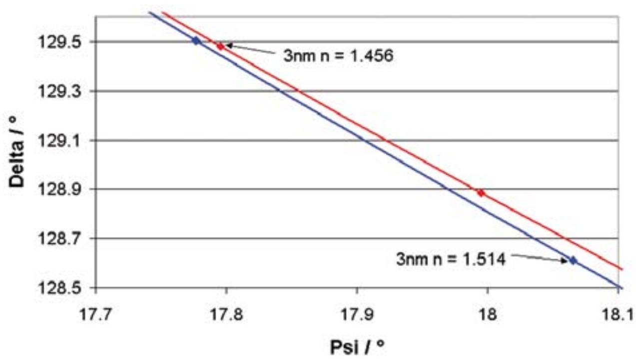
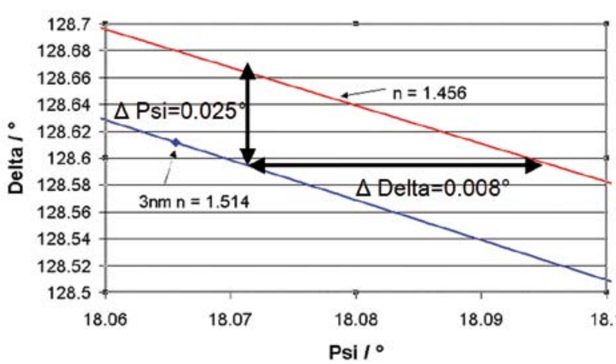


Serie 1 n=1.514 ; Serie 2 n=1.456 ; Serie 3 n= 1.460 ; Serie 4 n=1.498 ; Serie 5 n=1.535 ; Serie 6 n=1.572

We can note that the simulated Psi-Delta curves converge at the pseudo substrate value. The following expansion of the graph shows the Psi-Delta values of a 3nm layer with n=1.456 and n=1.514.



A further expansion shows the difference in the Psi-Delta plane between the curves n=1.456 and n=1.514. The difference between these curves is 0.025° in Psi and 0.008° in Delta.



The sensitivity of the UVISEL Spectroscopic Phase Modulated Ellipsometer was determined by 10 repeat measurements at the same point with an integration time of 5s, at λ=400nm. The results are showed in the table below.

	Ψ	Δ
Sensitivity	0.003°	0.003°

According to the found data for the 3nm layer, where the difference in Psi =0.025° and for Delta =0.008° and the measured sensitivity of the UVISEL, we can conclude that the refractive index n can be well resolved below 0.05 (n=1.514-1.456).

Experiments

To demonstrate the excellent sensitivity of the UVISEL Phase Modulated Spectroscopic Ellipsometer, the adsorption process of two non-ionic surfactants, Pentaethylene glycol monododecyl ether ($C_{12}E_{25}$) and Dioctadecyldimethylammonium bromide (DODAB) were studied at the silica-water and air-water interfaces respectively.

Experiment 1: Adsorption of C12E25 at silica-water interface

In order to characterize accurately the adsorption process of $C_{12}E_{25}$, the pseudo substrate consisting of 30 nm of thermal grown oxide deposited on c-Si was first measured in a liquid cell filled with water (figure1).

Measurements were performed by the UVISEL at an angle of 70° over a spectral range of 260 nm to 600 nm. Figure 2 shows the raw data (dots) along with the calculated data (solid line) for the pseudo substrate. A film thickness of 31.95 nm was found for the SiO_2 layer.

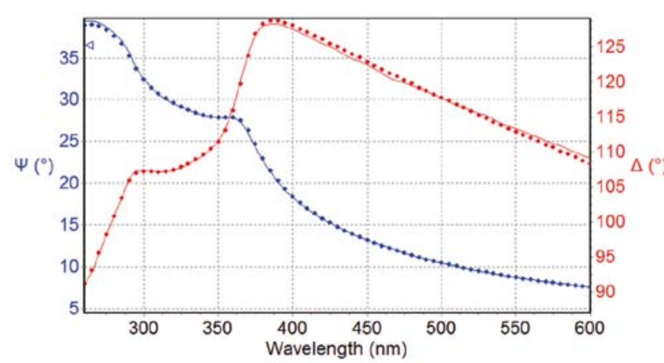


Figure 2: Ellipsometric data of the pseudo substrate

The kinetics of the $C_{12}E_{25}$ adsorption were monitored at a wavelength of 400 nm with a time resolution of 200 ms (figure 3). Results show clearly that the critical surfactant concentration (cmc) is reached at around 480 seconds. A classical oscillator model was applied to measure simultaneously the surfactant film thickness and the refractive index. The thickness of the surfactant was found equal to 3.59 nm and the optical constants derived across the full spectral range after the critical surfactant concentration is reached are shown in figure 4.

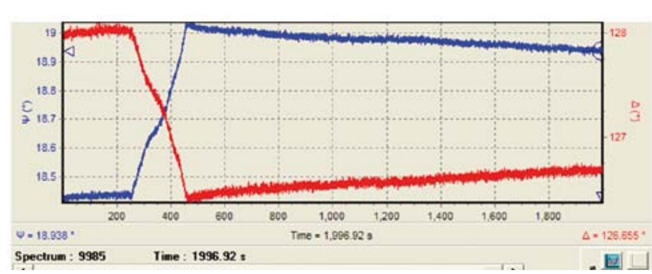


Figure 3: Adsorption of $C_{12}E_{25}$

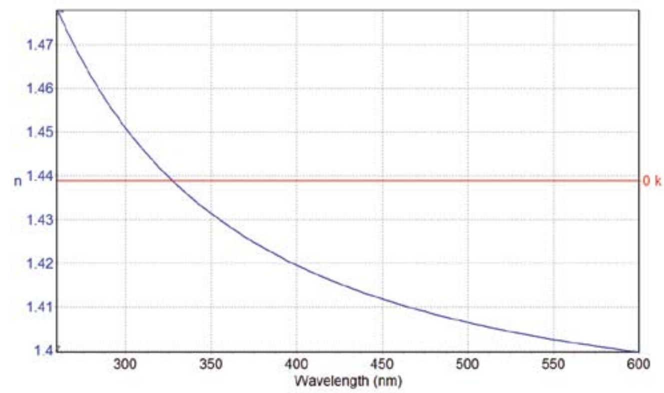


Figure 4: $C_{12}E_{25}$ optical constants

Experiment 2: Adsorption of DODAB at air-water interface

In order to characterize the adsorption process of the DODAB surfactant at the air-water interface, the angle of incidence of the UVISEL was changed to 54°, close to the Brewster angle for pure water substrates, and ellipsometric data were collected from 260 nm to 600 nm.

As previously, measurements on pure water were first collected and used as the pseudo substrate in the ellipsometric model. The film thickness and the optical constants of the DODAB surfactant were also extracted by using a classical oscillator model. Figure 5 shows a good fit agreement between the collected data (dots) and the model (solid line).

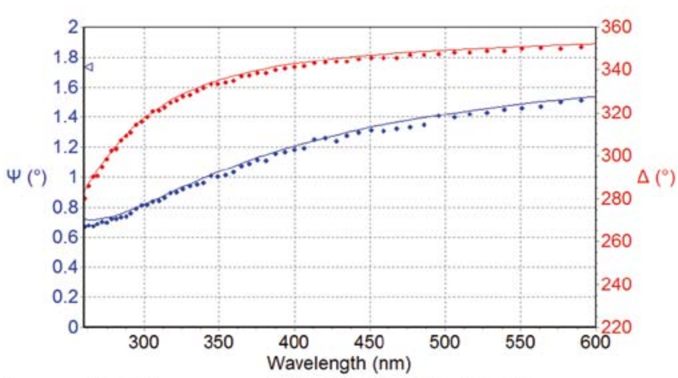


Figure 5: Fit agreement for DODAB film

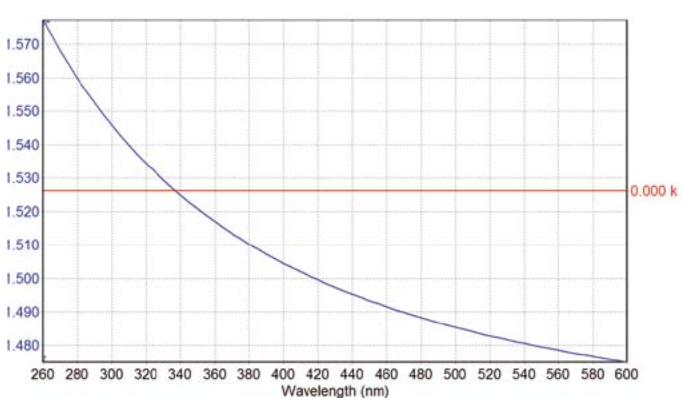


Figure 5: Fit agreement for DODAB film

As a result we can determine the thickness of the DODAB film to 1.44 nm and the optical constants as shown in figure 6.

Conclusion

This application note explains the methodology to characterize ultra thin films in a liquid environment by spectroscopic ellipsometry. The HORIBA Scientific UVISEL ellipsometer demonstrates an excellent sensitivity to determine both thickness and optical constants of ultra thin surfactant films without correlation.

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