Theses of Ph.D. dissertation

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# Nanoparticulate Langmuir and Langmuir-Blodgett films: preparation and characterisation

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## Introduction

Nanoparticles are widely used in different areas (e.g. emulsion stabilisation, photovoltaic devices, medical applications). Utilization of the particles is determined by the individual (electric, magnetic, wetting, etc.) properties of them and the structure the particles form. Nanoparticulate films can be formed by different – nanophysical and nanochemical – routes. The most effective methods among the wet chemical preparations are based on a layer-by-layer assembly of particles. One of them is the Langmuir-Blodgett (LB) technique which was introduced recently for the preparation of nanostructural films.

The main topic of the present work is the fabrication and characterization of nanoparticulate LB films composed of Stöber silica nanoparticles. Stöber silica has many advantageous properties. The isometric, nearly spherical particles can be prepared in a wide particle size range with narrow size distribution which makes them suitable for model investigations and technological applications.

## Aim of the work

The aim of this work is dual: on the one hand the intention was to develop techniques to fabricate particulate LB films with special optical properties, on the other hand the structure of the LB films - and of their precursor (Langmuir) films – was studied. According to this I focus my attention on four major topics: how films with antireflective properties can be prepared on transparent solid supports (1), how the water contact angle of partially wettable nanoparticles can be estimated (2), the contact angle related structure of the particulate films (3), and the relation of optical properties to the nano-scaled structure of the films (4).

## Methods

The experimental work consists of three distinct steps: preparation and characterization of the nanoparticles (1), preparation and characterization of the nanoparticulate monolayers (Langmuir films) at the water/air interface (2), fabrication and characterization of the LB films on various solid supports (3). In the following part of the text I provide a survey about the applied methods:

(1) For the experiments Stöber silica particles having narrow size distribution were synthesised in the 20-350 nm particle size range, with different wettability.

(2) The contact angle of the particles was determined by using a novel complex experimental procedure which is based on the thermodynamic analysis of the "non-dissipative" part of the surface pressure - area isotherms and on an optical method, scanning angle reflectometry (SAR, Fig. 1). For the interpretation of the SAR measurements two different optical models were fitted to the measurement data. The *uniform layer model* assumes the thin film as a single homogeneous layer, whilst the *gradient layer model* takes the particulate nature of the film into account. From the resultant parameters conclusions on the film structure were also drawn. As supplementary technique for the structure investigations Brewster-angle microscopy (BAM) was used (Fig. 1). For obtaining experimental data precisely and effectively, I made several modifications both on the hardware and the software of the experimental set-up.



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31. R.Cs. Tóth, N. Ábrahám, A. Deák, L. Naszályi, A. Ayral, F. Bosc, Z. Hórvölgyi: Fabrication of antireflective and self-cleaning coatings by wet colloid chemical methods (in Hungarian, Antireflexiós és öntisztító bevonatok előállítása nedves, kolloidkémiai eljárással), Műszaki Kémiai Napok '2006/Conference of Chemical Engineering, Veszprém, Hungary, 2006, Abstr. 40.

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33. N. Nagy, A.E. Pap, A. Deák, E. Horváth, A.L. Tóth, P. Fürjes, Z. Hórvölgyi, I. Bársony: Large area periodic silicon structures by a LB mask for photonic applications, Symposium K : Nanoscale self-assembly and patterning of the E-MRS 2007 Spring Meeting, Strasbourg, France, May 28 to June 1, 2007

34. N. Nagy, A. Deák, A. Hámori, Z. Hórvölgyi, M. Fried, P. Petrik and I. Bársony1: Comparative investigation of Stöber silica Langmuir-Blodgett films as optical model structures, 4th International Conference on Spectroscopic Ellipsometry, Stockholm, Sweden, June 11-15, 2007

35. L. Naszályi, R. Tóth, A. Deák, A. van der Lee, V. Rouessac, Z. Hórvölgyi, A. Ayral: Sol-gel synthesis of ZnO-based thin layers with enhanced optical properties, XIV International Sol-Gel Conference, September 2-7, 2007, Montpellier, France (accepted for oral presentation)

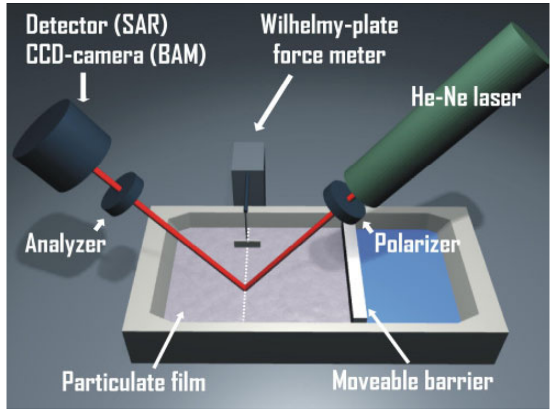


**Fig. 1.: Schematic picture of the instrument used for the measurements at the air/water interface**

(3) The Langmuir films were transferred on solid support by the LB technique, resulting in mono- and multilayered films. Besides the traditional multilayered films (the film is composed of particles with identical size) novel – complex – LB films were also prepared (the particle sizes are different in each layer of the multilayered film).

The build-up and structure of the LB films were studied by UV-Vis spectroscopy and SAR. Optical models were adapted, and the characterising parameters of the films (film thickness, effective refractive index) were determined for obtaining information about the optical properties and structure of the films.

## Results

1. A modified method for contact angle determination was applied and suggested based on the analysis of the “non-dissipative” part of the surface pressure (*Π*) – surface area (*A*) isotherms. This method provided more realistic contact angle values for the investigated nanoparticles than the traditional one. The resultant contact angles were found to be dependent on the size of Stöber silica particles (Fig. 2) which was attributed to the size dependent chemical composition of the particle-surfaces. *(Reference: 9)*

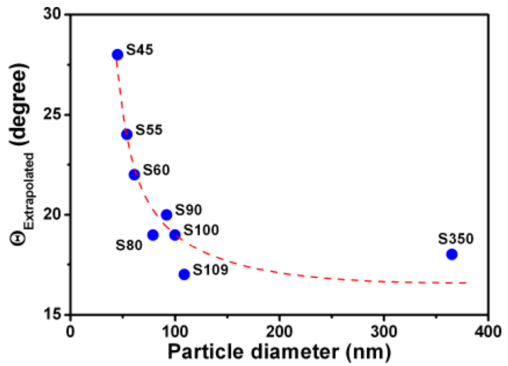


**Fig. 2.: Contact angles obtained for Stöber silica nanoparticles as a function of particle sizes (from a novel analysis of the Π-A isotherms).**

2. It was found that the relative compressibility and the relaxation degree of the Langmuir films increase as the particle sizes decrease. It was suggested, that the smaller the particles, the looser the structure of the Langmuir films which manifests itself in the aforementioned effects. It was established that the origin of the relaxation lies in the restructuring of the film after stopping the moving barrier.




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24. N. Nagy, A. E. Pap, A. Deák, E. Horváth, J. Volk, Z. Hórvölgyi, I. Bársony: Large area self-assembled masking for photonics applications, Physics of linear, nonlinear, and active photonic crystals/COST P11 meeting 2006, Brussel (2006)

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29. R.CS. Tóth, L. Naszályi, A. Deák, J. Szira, F. Bosc, A. Ayral, Z. Hórvölgyi: Functional properties of Langmuir-Blodgett films, 20th ECIS Conference, Budapest, 2006, Abstr. P6.36.

***Lectures***

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16. A. Deák, Z. Hórvölgyi: Nano-strukuturierte Dünnschichte von Silica Partikeln (Herstellung und optische Eigenschaften), 16. Frühlingsakademie 2004, München, Germany, 2004, Proc (Ed.: J. Ginsztler).

17. A. Deák, I. Székely, E. Kálmán, Zs. Keresztes, Z. Hórvölgyi: LB films composed of Stöber silica nanoparticles: structure and antireflective properties, PORANAL 2004, Balatonfüred, 2004, Abstr. 35.

18. A. Deák, I. Székely, Z. Hórvölgyi: Investigation of the optical properties of silica thin layers prepared by a wet colloid chemical method (in Hungarian: Kolloidkémiai eljárással előállított szilika vékonyrétegek optikai tulajdonságainak tanulmányozása), 10th Vegyészkonferencia 2004, Erdélyi Magyar Műszaki Tudományos Társaság, Kolozsvár, Romania, 2004, Proc. (Ed.: K. Majdik).

19. A. Deák, L. Naszályi, Z. Hórvölgyi: Preparation and characterization of particulate Langmuir-Blodgett films, 4th International Conference on Research and Education, Inter-Academia 2005, Wuppertal, Germany, Proc.

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21. A. Deák, Z. Hórvölgyi: Investigation of solid supported nanostructured thin films by scanning angle reflectometry, 5th Hungarian Conference and Exhibition on Materials Science, Testing And Informatics (V. OAAAKK), Balatonfüred, Hungary, 2005, Abstr. CD-ROM (ISBN: 963 219 274 5) O-III-04.

3. The reflectance curves provided by SAR measurements were evaluated using the uniform layer model by means of the effective refractive index ($n_{eff}$) and thickness of the films were determined for the Langmuir films of as-prepared silica particles. The $n_{eff}$ values were in good correlation with the contact angles obtained from the *Π-A* isotherms confirming my establishment that both the measurable $n_{eff}$ values (from the uniform layer model) and contact angles (from the *Π-A* isotherms) are defined by the same parameters: the immersion depth of particles and film structure. *(Reference: 9)*

4. a) As a results of this work a modified gradient layer model was suggested for the analysis of reflectivity curves. The experimentally determined particle-particle (p-p) distances (from the *Π-A* isotherms) were introduced in the model calculations. It was found that the immersion depth of the particles (contact angle) can be determined unambiguously in a broad particle-wettability range by using this modified model.

   b) It was also found that both the uniform and gradient layer models, in case of as-prepared particles, result in such film thickness values which are in good agreement with particle diameters determined by transmission electronmicroscopy. It was shown that the effective refractive indices determined from the uniform layer model were in a linear correlation with the h/D parameter (particle immersion depth/p-p distance), obtained from the gradient layer model (Fig. 3).

c) It has been shown, that in case of surface modified particles, the correlation between the two models breaks down as the particle size and hydrophobicity increase (Fig. 3). In these cases the film can not be considered homogeneous. *(Reference: 9)*

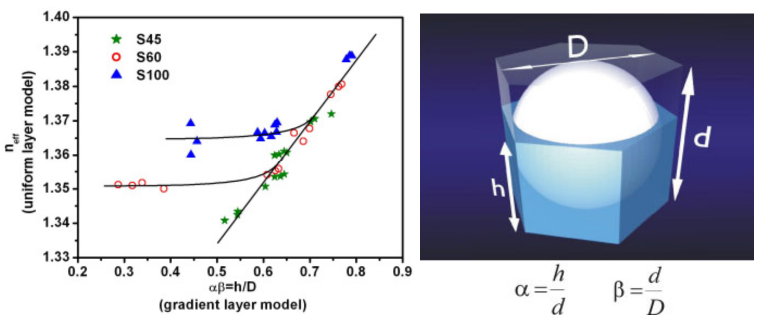


**Fig. 3: Correlation between the uniform and the gradient layer models: the effective refractive index (determined with the uniform layer model) as a function of the (α·β=h/D) parameter, obtained with the gradient layer model.**

5. a) It has been proved that Langmuir-Blodgett films from all of the prepared particle-samples can be fabricated on various solid supports (Fig. 4). Significant antireflective effect has been observed for all of the fabricated films by the optical spectroscopic investigations. The increased light transmittance of the prepared coatings can be explained in terms of the nano-scale structure of the particulate LB films. I developed an optical model to simulate the transmittance spectra of the films taking into account the dispersion of the substrate and that of the layer. This model describes the transmittance spectra of the LB films very well in the visible wavelength range.



9. A. Deák, E. Hild, A.L. Kovács, Z. Hórvölgyi: Contact Angle Determination of Nanoparticles: Film Balance and Scanning Angle Reflectometry Studies, Phys. Chem. Chem. Phys., accepted (2007) IF: 2.519

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5. N. Nagy, A. E. Pap, A. Deák, E. Horváth, J. Volk, Z. Hórvölgyi, I. Bársony: Large area self-assembled masking for photonics applications, Applied Physics Letters, 89 (2006) 063104. IF: 4.308

6. L. Naszályi, A. Deák, E. Hild, A. Ayral, A. L. Kovács, Z. Hórvölgyi: Langmuir-Blodgett films composed of size-quantized ZnO nanoparticles: fabrication and optical characterization, Thin Solid Films, 515 (2006) 2587. IF: 1.647

7. N. Nagy, A. E. Pap, A. Deák, J. Volk, E. Horváth, Z. Hórvölgyi, I. Bársony: Regular patterning of PS substrates by a self-assembled mask, Phys. Stat. Sol. (C), 4(6) (2007) 2021. IF: 0.860
8. A. Deák, E. Hild, A. L. Kovács, Z. Hórvölgyi: Characterisation of solid supported nanostructured thin films by scanning angle reflectometry and UV-Vis spectrometry, Mater. Sci. Forum, 537-538 (2007) 329. IF: 0.498


b) It has been shown for monolayers that the determined effective refractive indices increase with increasing particle hydrophobicity. I explained this effect in terms of the increased light scattering of the films which was attributed to the inhomogeneous layer structure.

c) The film thickness values determined from the transmittance spectra of the multilayered films showed that the films are getting denser as the number of layers increases. In case of bigger particles the deviation of the measured film thickness from the theoretical values (close-packed structure) tends to a limiting value as the number of layers increases. This was attributed to geometrical effects originating from the polydispersity of the particles. Additionally, a further consequence of this effect, the higher refractive index values for the multilayered samples, was explained in terms of light scattering from the uneven film surface. *(References: 2, 3, 8)*

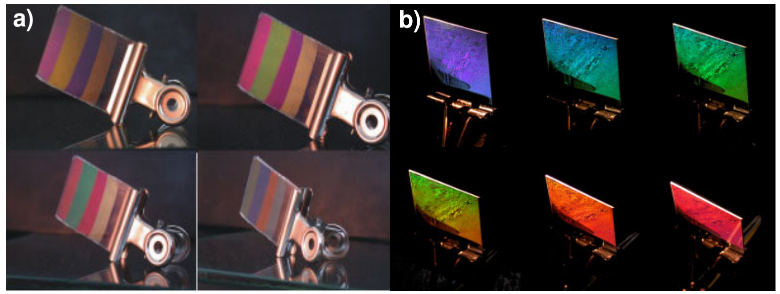


**Fig. 4.: Visualization of nanoparticulate LB films from different angles of observation: partially overlapping 5-layered LB film prepared from ca. 110 nm diameter particles on glass substrate (a) and monolayer of ca. 350 nm diameter particles on silicon substrate (b).**

6. I fabricated complex LB films which consist of different sized particles. The antireflective effect of these films exceeded significantly that of the traditional LB films (composed of same sized particles). It was found that the transmittance of the complex film at the transmittance minimum exceeded that of the substrate (Fig. 5). It was explained in terms of the refractive index gradient arising in the complex films, which also caused the increased transmittance in a broad wavelength range. *(References: 3, 10)*

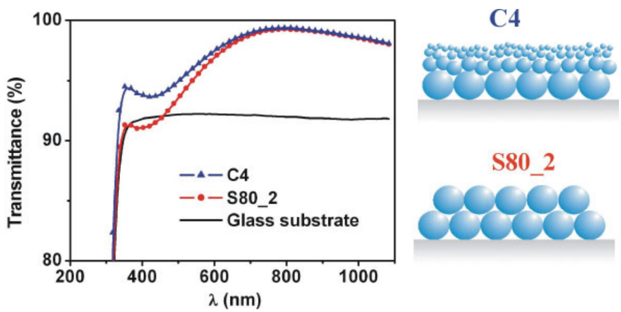


**Fig. 5.: Transmittance spectra of complex and traditional LB films having identical thickness but different structure (complex /C4/ and traditional /S80_2/ films).**

7. To the best of my knowledge this was the first attempt to use the scanning angle reflectometry method for investigating nanoparticulate LB films at solid/air interfaces. The results (film thickness and refractive indices) of SAR measurements were compared with those of UV-Vis spectroscopic measurements. It was found that scanning angle reflectometry is an effective tool for studying the structure of ultrathin coatings on solid supports. *(References: 6, 8)*



## Applications

Nanolitography: using nanoparticulate LB films it is possible to prepare periodic silicon structure over an area of several $cm^2$. The procedure can be carried out in a short time and cost efficiently. LB films can be used as masks during the ion-implantation of the silicon wafers prior to electrochemical and alkali etching that result in various crystalline silicon structures. The structure will depend on the type of the silicon wafer, of the ions, and the layer number of the LB-film [5,7].

Multifunctional films (antireflective and self cleaning, or superhydrophobic coatings): ongoing research aims the preparation of films that combine the advantageous properties of different nanoparticles. Using silica and ZnO nanoparticles in a multilayered film, it will exhibit both antireflective and photocatalytic properties, so beside the increased transmittance the film will show self-cleaning properties [29]. Creating an alternating layer structure from the above mentioned particles, it is possible to fabricate refractive index profile in a controlled way [10, 28]. Using the LB technique it is possible to prepare such coatings from ZnO or $TiO_2$ particles which show reversible wetting behaviour upon UV-irradiation [29]. Applying post synthetic surface modification of silica LB films superhydrophobic surfaces can be prepared [29]. These can also show an increased transmittance compared to the substrate.

Under proper adhesive conditions the particulate Langmuir films can be transferred on various – even on flexible – supports that gives an entry into the exciting world of flexible photonic structures and sensors.