University of Pécs

Physics Doctoral School
Nonlinear optics and spectroscopy program

Summary of the Ph.D. thesis

Optical characterization of plasmonic, periodic and combinatorial thin films for sensor applications

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Background and motivation

Our modern society could not exist without the precise manipulation of matter in the nanometer range. Without this, none of the latest achievements in the field of info-communication, optical and sensor applications could make our daily lives easier.

One of the most common tools for exploring the properties of nanometer structures and characterizing their quality in industrial environment is provided by ellipsometry [1]. Ellipsometry can be used to determine the optical properties and layer thickness (usually between 1-2 nm and a few microns) of thin films non-destructively and relatively quickly. The main application areas of ellipsometry include semiconductor devices, optical and biological coatings, protective coatings [2].

Compared to other thin film characterization methods [3], the unique properties of ellipsometry are its sensitivity, non-destructivity, velocity and its ability to monitor solid-liquid interfaces over a significant transparent wavelength range.

The number and prevalence of optical sensor designs are constantly increasing these days. Ellipsometry contributes to the investigation of these structures with its quantitative spectroscopic manner which is mainly based on the ability to measure phase. With the help of ellipsometer it is possible to interprete surface processes, and explore knowledge that contributes to the development of simpler sensor designs. For unique problems, an custom-made ellipsometer can be built from relatively simple and inexpensive hardware components utilizing adequate calibration and evaluation knowledge.

In the development of ellipsometric technique three main directions can be identified nowadays: (i) development of optical configurations, (ii) development of surface nanomaterials, (iii) development of theoretical and evaluation techniques for the interpretation of the measured optical signals. In my doctoral dissertation, I aimed to contribute to all three areas. I have developed nanostructures based on multilayers and combinatorial nanomaterials to increase the available sensitivity and versatility for spectroscopic applications. I modeled the spectra of these materials, their structural properties and their sensoric optical response.

One of the aims of my doctoral dissertation was to determine the composition-dependent optical properties of layer systems made with a new sample preparation method, combinatorial DC-magnetron deposition, demonstrating the unparalleled potential of this technique. The unique property of samples made by combinatorial deposition is that the composition (and even thickness) of the layer deposited on a substrate changes in a controlled manner along the position of the sample. The advantage of combinatorial sample preparation is that the full range of compositions can be produced within the same deposition process on the same substrate, thus greatly reducing the uncertain parameters of the experiment. The number of samples produced is also significantly reduced, making further experiments more manageable and less time consuming. Ellipsometric measurements provide an ideal measurement technique for these studies, as they can be performed with low lateral resolution, non-destructive, revealing the optical properties of the combinatorial samples.

First, I demonstrate the possibilities of combinatorial sampling on a material system with a long research history, namely a-SiGe. Then, an exciting combinatorial AgAl thin film sample is introduced which is motivated by biosensor applications. In the latter case, my goal - in addition to determining the optical properties of the combinatorial thin film - is to manipulate the sensitive wavelength range (spectral position of the resonance peaks) by changing the composition, so that multi-wavelength biosensor measurements can be performed even at one angle of incidence.

My other objective is to optically describe a biosensor structure operating in the ultraviolet range in a Kretschmann-Raether configuration (KR). Spectroscopic ellipsometry (SE) is again an ideal choice for this task, as the measurements can be performed in the appropriate spectral range, and the phase information of the light reflected from the structure contributes significantly to the of the sensing capabilities of the biosensor structure. For this reason, I investigated the sensing properties of a dielectric Bragg multilayer structure (BMS) in the ultraviolet range, both numerically and experimentally.

Subsequently, I compared the capabilities of the BMS structure with the capabilities of one of the most common plasmonic planar structures (Au thin film), highlighting the effect of imperfections stemming from the experimental setup (resulting from both the sample and ellipsometric configuration) on the sensing properties of the two systems.

Methods

In the dissertation, I investigated various layer structures deposited by electron beam deposition, RF- and DC magnetron sputtering with the help of SE. In the case of the latter deposition technique, the thin films were prepared by a micro-combinatorial method, as a result of which the entire x composition range ($0 \leq x \leq 1$) was realized on a sample. The layers were grown in an ultra-high vacuum system made of stainless steel using an up-scaled instrument [4]. This deposition method was originally used for special sample preparation dedicated for transmission electron microscopy investigations. In the arrangement used in this work, a plate moves over the sample, with a gap of 1 mm $\times$ 10 mm. The plate moves in fine steps, synchronously with changing the power of the two magnetron sources, so that the material flow of one of the targets at one end of the sample is 100%, which gradually decreases to 0% when the gap reaches the other end of the sample. In the case of the second target, the power is controlled in the same way in sync, and the material flow changes in the other direction compared to the first target.

Structures designed for sensor applications were also investigated in an ellipsometric arrangement optimized for studies using full internal reflection. These configurations have long been in use [5] and are popular even nowadays [6]. An important advantage of the method compared to the ”traditional” reflection arrangements is that the incident light beam does not pass through the examined liquid medium, so the refractive index perturbations in the liquid does not limit the sensitivity of the measurement. Another advantage is that the absorption of liquids in this case does not narrow the possible spectral detection range, thus in the case of an aqueous medium, for example, measurements can be made in the IR range also. Using an SPR array with ellipsometry, the layer formed on the surface of the gold layer can generally be traced with higher sensitivity than by simply using ellipsometry [7]. This combined measurement method is used in Total Internal Reflection Ellipsometry ([TIRE]) [8] or Plasmon Resonance Enhanced Elliphometry (SPREE) [9].

SE analysis of the structure was complemented by Rutherford backscattering spectrometry (RBS) [10], ERDA (Elastic recoil detection analysis) [11], TEM (Transmission electron microscopy). In addition, the obtained measurement results were also supported by numerical transfer matrix and finite element simulations.

Results

The following theses below summarize the results supported by publications as my own contribution to the present work:

1. I determined the dielectric functions of combinatorially created hydrogenated amorphous Si_xGe_{1-x} samples in the whole $0 \leq x \leq 1$ composition range by DC sputtering. I

determined the most appropriate optical model for the optical properties of the samples, and determined the change in the parameters in the model as a function of composition. I identified the linear n-ranges for each sample. [**S1**]

2. I determined the optical properties of a combinatorial Ag $_x$Al$_{1-x}$ thin film stabilized with a silicon nitride topcoat with a continuously variable composition and thickness in the whole 0$\leq$ x $\leq$ 1 composition range. I experimentally demonstrated its bionsensor performance in the UV-VIS-NIR wavelength ranges. [**S2**]

3. I performed a Kretschmann-Raether process-oriented ellipsometric measurement by using a Bragg dielectric layer structure with a resonant peak in the ultraviolet range. The sensing capabilities of the structure were experimentally demonstrated using solutions with different refractive indices as well as fibrinogen protein solution. I have also shown the effect of depolarization on the properties of the structure due to the angular broadening caused by the focused beam. [**S3**]

4. By using numerical calculations, I investigated the bulk refractive index sensitivities under different, non-ideal conditions in the cases of both a planar gold SPR sensor and

a Bragg dielectric layer structure. Consistent with the experimental results, I showed that in the case of the SPR sensor, a linear shift in the absorption peak is observed in a large wavelength range due to depolarization due to the broadening of the angle of incidence during the change of the bulk refractive index. [**S3**]

List of publication

Publications strictly related to the thesis

Articles published in peer-reviewed journals

[S1] **Kalas, B.**; Zolnai, Z.; Sáfrán, G.; Serényi, M.; Agócs, E.; Lohner, T.; Németh, A.; Nguyen, Q. K.; Fried, M.; Petrik, P., *Micro-combinatorial sampling of the optical properties of hydrogenated amorphous $Si_{1-x}Ge_x$ for the entire range of compositions towards a database for optoelectronics.* Sci Rep 10, 19266 (2020). (IF = 3.99)

[S2] **Kalas, B.**; Sáfrán, G.; Serényi, M.; Fried, M.; Petrik, P., *Optical properties of combinatorial Ag_xAl_{1-x} nanostructure for optical sensing applications.* Pozitív bírálat az *Applied Surface Science* folyóiratban (2022) (IF = 6.18)

[S3] **Kalas, B.**, Ferencz, K.; Saftics, A.; Czigány, Z.; Fried, M.; Petrik, P., *Bloch surface waves biosensing in the ultraviolet wavelength range – Bragg structure design for investigating protein adsorption by in situ Kretschmann-Raether el-*

lipsometry, Applied Surface Science, Volume 536, 2021, 147869 (IF = 6.18)

Other publications

Articles published in peer-reviewed journals

[**K1**] Jankovics, H.; Szekér, P.; Tóth, É.; Kakasi, B.; Lábadi, Z.; Saftics, A.; **Kalas, B.**; Fried, M.; Petrik, P.; Vonderviszt, F., *Flagellin-based electrochemical sensing layer for arsenic detection in water*, Sci Rep 11, 3497 (2021)

[**K2**] Bukovinszky, K.; Szalóki, M.; Csarnovics, I.; Bonyár, A.; Petrik, P.; **Kalas, B.**; Daróczi, L.; Kéki, S.; Kökényesi, S.; Hegedűs C., *Optimization of Plasmonic Gold Nanoparticle Concentration in Green LED Light Active Dental Photopolymer*, Polymers, 13, 275 (2021)

[**K3**] Pósa, L.; Molnár, Gy.; **Kalas, B.**; Baji, Z.; Czigány, Z.; Petrik, P.; Volk, J., *A Rational Fabrication Method for Low Switching-Temperature VO_2*, Nanomaterials, 11, 212 (2021)

[**K4**] Romanenko, A.; **Kalas, B.**; Hermann, P.; Hakkel, O.; Illés, L.; Fried, M.; Fürjes, P.; Gyulai, G.; Petrik, P., *Membrane-Based In Situ Mid-Infrared Spectroscopic Ellipsometry: A Study on the Membrane Affinity of Polylactide-co-glycolide Nanoparticulate Systems*, Anal. Chem., 93, 2, 981–991, (2021)

[**K5**] Lábadi, Z.; **Kalas, B.**; Saftics, A.; Illés, L.; Jankovics, H.; Bereczk-Tompa, É.; Sebestyén, A.; Tóth, E.; Kakasi, B.; Moldovan, C.; Firtat, B.; Gartner, M.; Gheorghe, M.; Vonderviszt, F.; Fried, M.; Petrik, P., *Sensing Layer for Ni Detection in Water Created by Immobilization of Bioengineered Flagellar Nanotubes on Gold Surfaces*, ACS Biomaterials-Science & Engineering 6 : 7 pp. 3811-3820. , 10 p. (2020)

[**K6**] Sáfrán, G.; Szász, N.; Dobrik, G.; **Kalas, B.**; Serényi, M., *Smart gas dosage by a peristaltic pump for reactive RF sputtering of composition spread combinatorial hafnium-oxy-nitride layers*, VACUUM 182 Paper: 109675 , 4 p. (2020)

[**K7**] Soleimani, S.; **Kalas, B.**; Horváth, Z.E.; Zolnai, Z.; Czigány, Z.; Németh, A.; Petrik, P.; Volk, J., *Optimization of co-sputtered $Cr_xAl_{1-x}N$ thin films for piezoelectric MEMS devices* Journal of Materials Science: Materials in electronics 31 : 11 pp. 8136-8143. , 8 p. (2020)

[**K8**] **Kalas, B.**; Agócs, E.; Romanenko, A.; Petrik, P., *In Situ Characterization of Biomaterials at Solid-Liquid Interfaces Using Ellipsometry in the UV-Visible-NIR Wavelength Range* Physica Status Solidi A-Applications and materials science 216 : 13 Paper: 1800762 , 9 p. (2019)

[**K9**] Petrik, P.; Romanenko, A.; **Kalas, B.**; Péter, L.; Novotny, T.; Perez-Feró, E.; Fodor, B.; Agocs, E.; Lohner, T.; Kurunczi, S.; Stoica M., Gartner M.; Hózer Z., *Optical Properties of Oxidized, Hydrogenated, and Native Zirconium Surfaces for Wavelengths from 0.3 to 25 μm - A Study by Ex Situ and In Situ Spectroscopic Ellipsometry* Physica Status Solidi A-Applications and materials science 216 : 8 Paper: 1800676 , 6 p. (2019)

[**K10**] Serényi, M.; Csík, A.; Hámori, A.; **Kalas, B.**; Lukács, I.; Zolnai, Zs.; Frigeri, C., *Diffusion and reaction kinetics governing surface blistering in radio frequency sputtered hydrogenated a-$Si_{1-x}Ge_x$ ($0 \leq x \leq 1$) thin films* Thin Solid Films 679 pp. 58-63. , 6 p. (2019)

[**K11**] Lohner, T.; **Kalas, B.**; Petrik, P.; Zolnai, Z.; Serényi, M.; Sáfrán, G. *Refractive Index Variation of Magnetron-Sputtered a-$Si_{1-x}Ge_x$ by "One-Sample Concept" Combinatory.* Appl. Sci. 2018, 8, 826. (IF = 1.68)

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[K17] Nádor, J.; **Kalas, B.**; Saftics, A.; Agócs, E.; Kozma, P.; Körösi, L. ; Székács, I.; Fried, M. ; Horváth, R.; Petrik, P. *Plasmon-enhanced two-channel in situ Kretschmann ellipsometry of protein adsorption, cellular adhesion and polyelectrolyte deposition on titania nanostructures* Optics Express 24 : 5 pp. 4812-4823. , 12 p. (2016)

Book chapter

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