Summary of the PhD thesis

Design, fabrication and application of plasmonic structures

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Introduction

Surface plasmons are collective resonant electron oscillations induced by light illumination of a dielectric-conductor (metal in most cases) boundary. Plasmonics is a branch of photonics investigating these oscillations, studying the emergence, characteristics and means of their modification. The EM-field of surface plasmons decays exponentially if measured perpendicularly to the boundary and this decay length is smaller than the propagation length, which is in the order of 10 nm - 100 μm depending on the illuminating light wavelength and on material properties. Due to the development of miniaturization the fabrication of such small surface structures is possible, which can alter the resonance characteristics of plasmons. Based on these small features, surface structures can be fabricated which are able to function as plasmonic devices even though there are inherent energy losses caused by propagation.

The instruments based on the unique characteristics of plasmons have large field of applications. Wavelength-scaled plasmonic structures were demonstrated to act as like optical elements, e.g. flat mirrors. Plasmonic structures can be used in data storage, microscopy and for increasing the efficiency of photovoltaic elements. Another important filed of applications is the fabrication of plasmonic sensors to detect different biological materials, these are capable of detecting even single molecules. Significant part of surface features used in biosensors is the class of periodic structures, e.g. plasmonic crystals (which are analogous to photonic crystals) or plasmonic meta-materials.

The wave vector of a plasmon is larger than of a photon having the same frequency according to the dispersion relation of the plasmon, so the plasmons can be generated only if this difference is compensated. This can be addressed in different ways, among them the most common experimental solution is the use of a prism. With application of a grating light can be coupled into and out from the plasmonic systems, meaning that plasmonic circuits can be fabricated. This leads to the development of electronic devices much smaller than the ones used nowadays, which is a future prospect for light-based photonic circuits.

The controlled fabrication of plasmonic structures is crucial for many applications of plasmonics, many scientific and technical problem can be solved with appropriate plasmonic patterns. Laser-based material processing methods are parallel techniques, large areas can be structured in a single step. In laser-based lithography methods the permanent surface modification depends on the parameters of the applied laser and on the material properties. The physical process responsible for surface structure development can be the ablation (material removal and/or relocation) or a photochemical change in the material (photoresist) or the combination of the two phenomena. The methods based on ablation usually are one-step and these are considered as fast and simple techniques, but the fabrication of complex structures is challenging. Complex structures can be prepared with multi-step lithography of photoresists. These in most cases require elaborate equipment and thorough knowledge, and appropriately high resolution structuring can be performed in high level clean room environments, which is not widely available. Structures with wavelength range size can be prepared using laser interference lithography methods, which can be used in different fields of science and industry. The disadvantage of these methods is that nanometric features can be made only via hardly controllable self-organized phenomena caused by the diffraction limit.

Colloid sphere lithography is capable of resulting in well defined small structures. The light illuminating such spheres is concentrated below them modifying the substrate surface. In most cases, the spheres are hexagonally closely packed on the surface, so the result inherits this symmetry. The result of the illumination is the function of the sphere and substrate material properties and of the illumination parameters. In multi-step processes the colloid particles or the structured surface is covered with additional material, but these patterns have always hexagonally symmetry. Fabrication of linear patterns is possible only with the use of masks or with the alteration of the chemical forces between the spheres.

As a result plasmonic detectors investigation, at the beginning of the 1990s emerged the first commercial detectors based on surface plasmon resonance spectroscopy. More companies followed the Swedish Biacore, so thanks to the continuous developments, detection of wide variety of biomaterials ranging from allergens and cancer markers (Spreeta) through antibodies (Autolab Esprit) to bacteria (Biacore 3000) are possible. These devices measure the optical properties of a material circulated in a flow pipe and after appropriate calibration the amount of material is determined. With multichannel devices more measurements can be realized simultaneously, but these require complicate setup for materials circulation.

Plasmonic detectors based on the lab-on-chip designs can be less complicated. The concept of such a detector is that different small surface areas are prepared differently to observe a specific material, and the light in- and outcoupling is ensured, e.g. via plasmonic nanostructures. These detectors can operate even in dry environment and can be prepared via versatile lithographical procedures.

Based on this idea, during my work I have studied whether metal and polycarbonate gratings can act as biodetectors. Advancing from the simple grating surfaces towards more complex design I have studied experimentally the fabrication of linear plasmonic structure prepared with the use of a composite mask. I have studied with finite element modeling the possibilities of an optical lithography method which has fewer steps, it is less complicated and is capable of controlling the linear structure. I have searched how the plasmonic structures can be used for the detection of streptavidin.

Objectives

Studying the literature concerning periodic and plasmonic structures one can conclude that application of complex structures consisting of wavelength-scaled arrays of components with size below the diffraction limit is very large, but there is demand for further development. The methods used to prepare such complex structures are generally time consuming and the high cost are not a marginal factor. Based on these, research for novel techniques for fabrication of periodic and complex structures is necessary.

The different fields of nanophotonics and nanoplasmonics require special complex structures. Several theoretical methods are available to describe the effect of plasmonic structures on the optical properties of a surface. The general use of nano- and plasmonic structures is preceded by the experimental and theoretical study of their properties, the testing of the surfaces as biosensors.

According to this, my objectives were as follows:

My first goal was to study the surface quality of gold-silver bimetal grating prepared with laser illumination, which is needed to determine the ideal layer thicknesses for biodetection. I intended to show with surface plasmon resonance spectroscopy (SPRS) that the bimetallic grating can be used to detect streptavidin.

My second objective was to determine those laser structuring parameters, which can be used to tune the surface morphology of a polymer layer spin-coated on bimetallic film. Using SPRS I aimed to study the use of polycarbonate gratings as biodetectors and to investigate the change of sensitivity due to the conjugation of gold particles to the streptavidin.

My third objective was the fabrication of a composite mask by spin-coating Stöber-silica colloid spheres on polymer master grating and with the illumination of this mask fabrication of linear arrays. I planned to test the fabricated linear array as a sensor for detection of dielectric materials.

My fourth goal is the study of the illumination by two interfering beams of gold and Stöber-silica colloid sphere monolayers with the use of finite element modeling. I intended to examine the dependence of the structure parameters of the resulting pattern on the illumination conditions and monolayer characteristics. I planned to investigate theoretically the plasmonic properties of linear complex structures.

Methods

I used the two beam interference method to prepare gratings in bimetal films and in polycarbonate films spin-coated onto bimetal films. The use of simple components is the advantage of this method, low cost fabrication of appropriately variable structure is possible. The interference of two coherent beams having the same wavelength and plane of incidence results in a linear interference pattern. In experiments I used two setups to fabricate gratings. The first was based on the use of mirrors to produce an interference pattern on the substrate surface, the other was the master grating based arrangement. Considering the advantages and disadvantages of these methods, I used the first one to fabricate bimetal gratings which require higher fluence, and for lower fluence need of polycarbonate covered sample the master grating based arrangement was more suitable. The light source was the fourth harmonic beam of a Nd:YAG pulsed laser (Spectra Physics Quanta Ray Pro, 10 Hz) with λ_{FH} = 266 nm wavelength and τ =10 ns pulse length.

The sample substrate was an interferometrically flat NBK7 glass (Geodasy, EKSMA) and gold-silver bimetallic films were evaporated onto these having different thickness combinations. To prepare polymer gratings, a polycarbonate layer was spin-coated onto the bimetal film. The lower damage threshold of polycarbonate makes it possible to fabricate well-controlled gratings with relatively low laser fluence. The spin-coating technique was used to depose Stöber-silica colloid spheres into the valleys of the polycarbonate gratings. The adhesion of grating valleys and the periodic topography ensures that the colloid particles are well ordered. This complex mask consisting of colloid spheres in the grating valley was illuminated with KrF excimer laser. The generated linear hole array after atomic force microscope (AFM) and SPRS investigation was recovered with silica colloid spheres or polycarbonate. For the modeling of colloid sphere lithography I used gold and Stöber-silica particles, in the experiments I used the silica spheres.

In a modified Kretschmann-arrangement the attenuated total reflection based SPRS method was used to study the layer combinations and the fabricated samples were studied. The topography of the surfaces was measured with AFM. The resolution of modern AFMs is below the diffraction limit, enables to study the sample surfaces in such detail that with other methods is only partially available or not available at all. I used the tapping mode option during the measurement, in this configuration the cantilever oscillates above the sample surface without contact. This method is adequate to measure sensitive materials like biomaterials or even living cells. The phase map gives information on the different materials on the surface by mapping the change of the phase of cantilever oscillation compared to the driving signal.

The surfaces prepared were used to detect biomaterials, we studied detection of small amount of unlabeled streptavidin and streptavidin labeled with gold particles. The attachment of biomaterials was made always out of freshly prepared solutions. The non-covalent binding between streptavidin and biotin is strong, so the used amount of biotin determines the adhered amount of streptavidin, and thus the amount of labeling gold particles is controllable

Theoretical methods were used to analyze the measured SPRS spectra and to model the pattern available below interference illuminate colloid spheres. The finite element method (FEM) is a numerical calculation procedure, which enables to calculate the solutions of predefined partial differential equations. The equations are solved at the nodes of a mesh, and the results are extrapolated to other regions. I used FEM to investigate illumination by two interfering beams of gold and Stöber-silica colloid sphere monolayers and to model the near-field effect of gold labeling particles conjugated to streptavidin molecules.

I used the analytical transfer matrix method (TMM) to help in the design and modeling of the surface structures and to analyze the measured SPRS resonance curves. Using the TMM method reflection and transmission of thin films and stack of thin films can be calculated. The essence of this method is that the reflection, transmission and absorption can be calculated at a boundary of two layers with an appropriate transfer matrix, for multiple layers a matrix for the whole system can be given.

New scientific results

I summarize the new scientific results as follows:

1.(a) Studying 900 nm periodic gratings prepared on glass substrate covered with bimetal layers consisting of silver and gold thin films with different thicknesses I have proven that the quality of the surface structure is a function of the composing metal layers thickness [T1].

1.(b) Based on the angle dependent surface plasmon resonance spectroscopy measurement in a modified Kretschmann-arrangement of bare and streptavidin ad-layer covered bimetal gratings I have shown that the periodically modulated bimetal films can be used as plasmonic detectors [T1].

2.(a) I have shown that the topographic modulation generated on a polycarbonate dielectric layer spin-coated onto bimetal thin film can be tuned by changing the experimental parameters (applied laser pulse number, fluence, polarization) in a master-grating based lithography setup [T2].

2.(b) I have proven that linear polycarbonate grating covered bimetal layers can be used as plasmonic detectors to observe small amount of streptavidin with surface plasmon resonance spectroscopy method. I proved with SPRS and finite element modeling that the labeling of streptavidin with colloidal gold particles enhances the sensitivity of detection [T3].

3.(a) I have proven that linear pattern of holes can be generated using a multistep method by laser illumination of a composite mask consisting of 250 nm és 500 nm diameter Stöber-silica colloid spheres spin-coated into the valleys of a 416 nm and 833 nm periodic linear polycarbonate grating [T4].

3.(b) By recovering the linear hole-array with the polycarbonate and Stöber-silica I have proven that the surface fabricated with the composite mask can be used to detect dielectric layers [T4].

4.(a) I have proven with finite element modeling that the two-beam interference illumination of gold and Stöber–silica colloid sphere monolayers placed on thin gold films that linear hole-array can be generated via optical method. I have shown that by changing the orientation of the interference maxima measured to (1, 0, 0) crystallographic direction of the monolayer of spheres placed at a *d* distance between each other linear array of nanoobjects can be generated having period commensurate with [*d/2*]/[$\sqrt{3}d/2$] and positioned at the [*d/*$\sqrt{3}d$] distance along the maxima. I have shown that in case of illumination by two interfering beams the near-field under the spheres is always larger than in case of homogeneous illumination regardless 532 nm and 400 nm wavelength and the circular or linear polarization is applied [T5, T6].

4.(b) In case of gold spheres I have proven that the size of the features generated by 532 nm illumination the size of the structure decreases with the sphere diameter. With the finite element modeling of the transmittance spectra of hexagonal and linear patterns of single holes and hole doublets I have proven that the geometry of holes with ~10 nm size and the array of these can alter the transmittance spectrum of the gold thin film containing them, which can be helpful in specific biosensor applications [T5].

4.(c) Illuminating Stöber-silica spheres having 500, 250 and 100 nm diameter with circularly polarized homogeneous beam the generated nano-objects are circular regardless the wavelength, while for linear polarization these show larger ellipticity for 532 nm wavelength, than for 400 nm. Using two-beam interference illumination linear arrays of elliptical holes can be generated with linearly polarized beams, while for circular polarization array of more cylindrical nanoholes and nano-crescents can be achieved [T6].

Publications

Peer reviewed journal publications related to the theses:

[T1] M. Csete, A. Kőházi-Kis, Cs. Vass, Á. Sipos, G. Szekeres, M. Deli, K. Osvay, Zs. Bor: *"Atomic force microscopical and surface plasmon resonance spectroscopical investigation of sub-micrometer metal gratings generated by UV laser based two-beam interference in Au-Ag bimetallic layers"*, Applied Surface Science, **254**(19), p. 7662-7671 (2007).

[T2] M. Csete, Á. Sipos, A. Kőházi-Kis, A. Szalai, G. Szekeres, A. Mathesz, T. Csákó, K. Osvay, Zs. Bor, B. Penke, M. A. Deli, Sz. Veszelka, A. Schmatulla, O. Marti: *"Comparative study of sub-micrometer polymeric structures: Dot-arrays, linear and crossed gratings generated by UV laser based two-beam interference, as surfaces for SPR and AFM based bio-sensing"*, Applied Surface Science **254**(4), p. 1194-1200 (2007).

[T3] Á. Sipos, H. Tóháti, A. Mathesz, A. Szalai, Sz. Veszelka, M. A. Deli, L. Fülöp, A. Kőházi-Kis, M. Csete, Zs. Bor: *"Effect of nanogold particles on coupled plasmon resonance on biomolecule covered prepatterned multilayers"*, Sensor Letters **8**, p. 512-520 (2010).

[T4] Á. Sipos, H. Tóháti, A. Szalai, A. Mathesz, M. Görbe, T. Szabó, M. Szekeres, B. Hopp, M. Csete, I. Dékány: *"Plasmonic structure generation by laser illumination of silica colloid spheres deposited onto prepatterned polymer-bimetal films"*, Applied Surface Science 225(10) p. 5138-5145 (2009).

[T5] M. Csete, Á. Sipos, A. Szalai, G. Szabó: *"Theoretical Study on Interferometric Illumination of Gold Colloid Sphere Monolayers to Produce Complex Structures for Spectral Engineering"*, IEEE Photonics Journal, 4(5) p. 1909-1921 (2012).

[T6] Á. Sipos, A. Szalai, M. Csete: *"Integrated lithography to prepare periodic arrays of nano-objects"* Applied Surface Science, online megjelent, DOI: 10.1016/j.apsusc.2012.11.078 p. 1-6. (2012).

Other publication in a peer-reviewed journal:

1. H. Tóháti, Á Sipos, G. Szekeres, A. Mathesz, A. Szalai, P. Jójárt, J. Budai, Cs. Vass, A. Kőházi-Kis, M. Csete, Zs. Bor: *"Surface plasmon scattering on polymer-bimetal layer covered fused silica gratings generated by laser-induced backside wet etching"*, Applied Surface Science 255(10) (2009) p. 5130-5137.
2. Deli MA, Veszelka S, Csiszár B, Tóth A, Kittel A, Csete M, Sipos A, Szalai A, Fülöp L, Penke B, Abrahám CS, Niwa M.: *"Protection of the Blood-Brain Barrier by Pentosan Against Amyloid-ß-Induced Toxicity",* Journal of Alzheimers Disease 22 (2010) p. 777–794.
3. M. Csete, Á. Sipos, F. Najafi, X. Hu and K. K. Berggren: "*Numerical method to optimize the polar-azimuthal orientation of infrared superconducting nanowire single-photon detectors*", Applied Optics, Vol. 50/31 (2011) p. 5949-5956.
4. György B, Módos K, Pállinger E, Pálóczi K, Pásztói M, Misják P, Deli MA, Sipos A, Szalai A, Voszka I, Polgár A, Tóth K, Csete M, Nagy G, Gay S, Falus A, Kittel A, Buzás EI: *"Detection and isolation of cell-derived microparticles are compromised by*

protein complexes due to shared biophysical parameters", Blood 117(4) (2011) p. E39-E48.

5. M. Merő, Á. Sipos, G. Kurdi, and K. Osvay: *"Generation of energetic femtosecond green pulses based on an OPCPA-SFG scheme",* Optics Express 19(10) (2011) p. 9646-9655.

6. M Csete, A Szalai, Á Sipos, G Szabó: *"Impact of polar-azimuthal illumination angles on efficiency of nano-cavity-array integrated single-photon detectors"* Optics Express 20(15) (2012) p. 17065-17081.

7. M Csete, Á Sipos, F Najafi, K K Berggren: *"Optimized polar-azimuthal orientations for polarized light illumination of different superconducting nanowire single-photon detector designs"* Journal of Nanophotonics 6(1) (2012) p. 063523.

8. Edit Csapó, Rita Patakfalvi, Viktória Hornok, László Tamás Tóth, Áron Sipos, Anikó Szalai, Mária Csete, Imre Dékány: *"Effect of pH on stability and plasmonic properties of cysteine-functionalized silver nanoparticle dispersion"* Colloids and Surfaces B-Biointerfaces 98 (2012) p. 43-49.

9. A Szalai, Á Sipos, E Csapó, L Tóth, M Csete, I Dékány: *"Comparative study of plasmonic properties of cysteine functionalized gold and silver nanoparticle aggregates"* Plasmonics (2012) in press DOI: 10.1007/s11468-012-9420-y p. 1-10.

10. T. Csizmadia, B. Hopp, T. Smausz, J. Kopniczky, I. Hanyecz, Á. Sipos, M. Csete, G. Szabó: "*Possible application of laser-induced backside dry etching technique for fabrication of SERS substrate surfaces*", Applied Surface Science (2012) in press, DOI: 10.1016/j.apsusc.2012.12.037, p. 1-7.

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11. M. Csete, Á. Sipos, A. Szalai, A. Mathesz, M. A. Deli, Sz. Veszelka, A. Schmatulla, A. Kőházi-Kis, K. Osvay, O. Marti, Zs. Bor: "Bio-sensing based on plasmon-coupling caused by rotated sub-micrometer gratings in metal-dielectric interfacial layers" Advanced Environmental, Chemical, and Biological Sensing Technologies V. Edited by Vo-Dinh, Tuan; Lieberman, Robert A.; Gauglitz, Günter. Proceedings of the SPIE, Volume 6755, pp. 67550X (2007).)

12. Mária Csete; Áron Sipos; Faraz Najafi; Karl K. Berggren: "Polar-azimuthal angle dependent efficiency of different infrared superconducting nanowire single-photon detector designs" Infrared Sensors, Devices, and Applications; and Single Photon Imaging II, Edited by Paul D. LeVan; Ashok K. Sood; Priyalal S. Wijewarnasuriya; Manijeh Razeghi; Jose Luis Pau Vizcaíno; Rengarajan Sudharsanan; Melville P. Ulmer; Tariq Manzur, Proceedings of the SPIE, Volume 8155, pp. 81551K (2011)

13. Áron Sipos, Anikó Szalai, Mária Csete_"Integrated lithography to prepare arrays of rounded nano-objects" In: William M Tong, Douglas J. Resnick (szerk.) Alternative Lithographic Technologies IV., Proceedings of SPIE 8323, SPIE - The International Society for Optical Engineering, pp. 83232E-1-83232E-10. (2012)