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Coupled long range surface plasmons for the investigation of thin films and interfaces

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ABSTRACT

We report a new approach for the investigation of thin films and interfaces based on the spectroscopy of coupled long range surface plasmons (cLRSPs). These modes are supported by a symmetrical layer structure with two metallic waveguides along which long range surface plasmons (LRSPs) propagate. For sufficiently small gap between the metallic waveguides, coupling between these LRSPs is established which gives rise to two new cLRSP modes. In surface plasmon resonance (SPR) sensors, cLRSPs can simultaneously probe events occurring on the sensor surface that are accompanied with refractive index changes. As the evanescent field of the two cLRSPs exhibits different penetration depths into the sensed medium on the top of the sensor surface, the spectroscopy of cLRSPs allows for the interrogating of the distribution of refractive index changes perpendicular to the surface. This feature advances the performance of current SPR sensors. We demonstrate the potential of the spectroscopy of cLRSP in an application in which we investigated swelling of thin hydrogel films and the diffusion of protein molecules into these gels.

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1. Introduction

Various optical methods were developed for *in situ* characterization of thin films and interfaces including absorption and vibration spectroscopy [1], ellipsometry [2], spectroscopy of waveguide [3] and surface plasmon (SP) modes [4–7] and surface plasmon-enhanced fluorescence spectroscopy (SPFS) [8]. In surface plasmon resonance (SPR) sensors utilizing the spectroscopy of SPs, surface plasmons are excited on a metallic sensor surface to probe events accompanied with refractive index changes on its top [9]. In these devices, the refractive index changes are detected through induced variations in the propagation constant of surface plasmons. In sensors employing SPFS, surface plasmons are used for the excitation of fluorophore labels anchored to investigated species such as biomolecules or polymers adhered to the sensor surface [8,10]. This method takes advantage of the enhanced intensity of electromagnetic field upon the resonant excitation of SPs which greatly increases the measured fluorescence signal.

Only recently, long range surface plasmons (LRSPs) have been introduced to optical sensors [11–13]. LRSPs are supported by a thin metallic film embedded between two dielectrics with similar refractive indices [14]. LRSPs can propagate along metallic films with an order of magnitude lower damping than conventional SPs.

Therefore, the excitation of LRSPs is associated with a narrower resonance and larger enhancement of intensity of the electromagnetic field which can advance both SPR and SPFS-based sensors [15].

In this communication, we report a new approach for the investigation of thin films based on the spectroscopy of coupled long range surface plasmons (cLRSPs). These modes can be excited in a refractive index symmetrical layer structure with two metallic films along which LRSPs propagate. Through coupling of LRSPs across the gap between the metallic films, two new cLRSP modes are established. The excitation of cLRSPs allows for simultaneous probing the sensor surface by their evanescent fields which exhibit different penetration depths into sensed medium. This feature enables interrogating the distribution of measured events perpendicular to the sensor surface and, for instance, allows for simultaneous measurement of the thickness and refractive index of studied thin films. Contrary to other reported approaches which were introduced to SPR sensors such as two-color SPR [4], multiple surface plasmon spectroscopy [16], spectroscopy of Bragg-scattered surface plasmons [7] or spectroscopy of long range and short range surface plasmons [6], the presented approach allows for the measurement at a single wavelength. Therefore, spectroscopy of cLRSP offers the advantage of the observation of refractive index variations that is not affected by the dispersion of involved materials. In addition, the excitation of cLRSPs can be implemented to other SPR-based techniques for the investigation of thin films and interfaces such as SPFS.

In order to demonstrate the potential of the reported approach, we implemented the spectroscopy of cLRSPs to a SPR sensor

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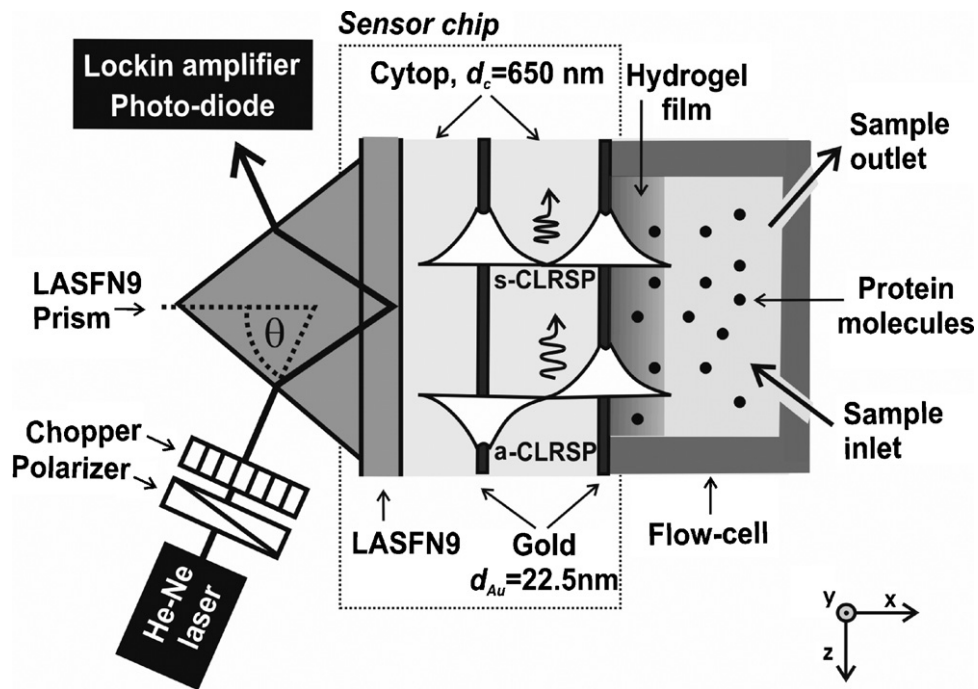


Fig. 1. Optical setup of a SPR sensor utilizing the spectroscopy of cLRSPs.

and applied the developed instrument for the investigation of the swelling of thin hydrogel films and the diffusion of protein molecules into these gels.

2. Experimental

In the experiments, we used an optical setup depicted in Fig. 1 for the excitation of cLRSPs. A light beam emitted from a He–Ne laser ($\lambda = 633 \text{ nm}$) passed through a polarizer and it was coupled to a LASFN9 glass prism with a sensor chip optically matched to its base. The sensor chip consisted of a LASFN9 glass slide that was successively coated with low refractive index polymer and gold layers as described in reference [15]. The thickness and refractive index of the low refractive index polymer layers (Cytop, CTL-809M, ASAHI Inc., Japan) were of $d_c = 650 \text{ nm}$ and $n_c = 1.3395$, respectively. Gold layers were deposited with the thickness of $d_{Au} = 22.5 \text{ nm}$ and their refractive index was determined as $n_{Au} = 0.3 + 3.5i$ [15]. On the top gold surface, a thin UV-cross-linkable hydrogel layer was deposited. A hydrogel based on *N*-isopropylacrylamide was used, the copolymerisation of *N*-isopropylacrylamide, methacrylic acid and 4-methacryloyloxy benzophenone as well as the immobilization of this copolymer on gold surfaces was described elsewhere [17]. The thickness of the dry hydrogel layer was 83 nm as measured with a surface profiler. Against the sensor chip surface, a flow-cell was attached to contain aqueous samples. The assembly of the prism, sensor chip and the flow-cell was mounted on a rotation stage to control the angle of incidence of the light beam. The intensity of the light beam reflected light from the sensor surface was measured using a photodiode and a lock-in amplifier. The angular reflectivity spectra as well as the time evolution of the resonant angles of incidence were recorded using the home-developed software Wasplas.

3. Results and discussion

Within the described layer structure, LRSPs can propagate along both metal films for an aqueous medium in the flow-cell. The

refractive index of water $n_b = 1.333$ is close to that of the Cytop polymer n_c which generates the required refractive index symmetrical geometry. As LRSPs on each metal film exhibit similar propagation constants and their electromagnetic fields partially overlap, coupling between them is established. This interaction gives rise to two new coupled LRSP modes with symmetrical and anti-symmetrical distribution of magnetic intensity across the layer structure. As shown in Fig. 2, the symmetrical mode (s-cLRSP) and anti-symmetrical mode (a-cLRSP) exhibit different penetration depths of $L_p = 364$ and 950 nm , respectively, into the aqueous medium. Therefore, these modes are unequally sensitive to refractive index changes occurring in different distances from the sensor surface. As seen in Fig. 3 and Fig. 4, the excitation of a-cLRSP and s-cLRSP modes is manifested by two distinct resonant dips in the reflectivity spectrum centered at $\theta_s = 47.63^\circ$ and $\theta_a = 49.63^\circ$, respectively.

Further, we investigated two hydrogel films noted as A and B which were cross linked with a UV light (wavelength of 365 nm and

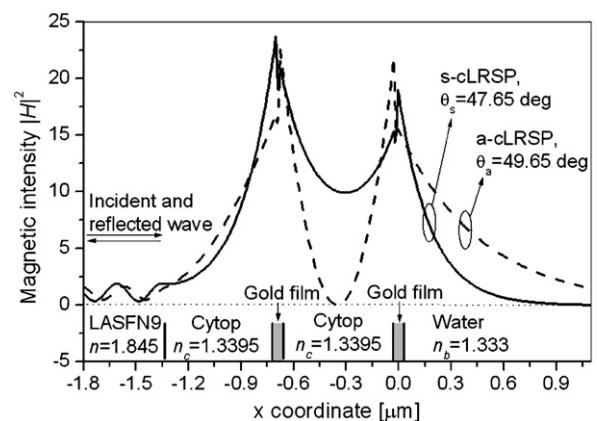


Fig. 2. The distribution of magnetic intensity field of symmetrical (solid line) and anti-symmetrical (dashed line) cLRSP mode.

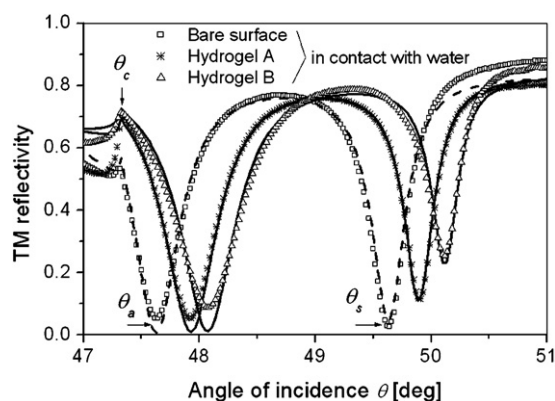


Fig. 3. Angular reflectivity spectra measured upon the probing a hydrogel layer A cross linked for 15 min (asterisk), hydrogel layer B cross linked for 40 min (triangle) compared to spectra measured for a bare gold surface (square) in contact with water. Fitted reflectivity spectra are shown for each sample (lines).

irradiation power $0.1 \text{ J cm}^{-2} \text{ min}^{-1}$) for 15 and 40 min, respectively. Firstly, we incubated each hydrogel film in water for 1 h and measured the angular reflectivity spectra. To characterize a hydrogel layer on the top gold surface, we fitted the corresponding reflectivity spectra with transfer matrix-based model implemented in the home-developed software Winspall. By fitting the angular positions of the resonant dips θ_s and θ_a and the critical angle θ_c , we determined the thickness d_h and the refractive index n_h of a hydrogel film and the refractive index of the bulk aqueous sample n_b . In these fits we assumed that the refractive index n_h is constant through the hydrogel film. The fitting of the measured curves in Fig. 3 revealed that the thickness of the hydrogel B ($d_h = 612 \text{ nm}$) was lower than that for hydrogel A ($d_h = 682 \text{ nm}$) and that the refractive index of the hydrogel B was larger ($n_h = 1.3521$) than the one of the hydrogel A ($n_h = 1.3438$). These results indicate that for the higher cross linking time a denser and less swollen hydrogel film is prepared. In addition, we investigated the swelling of the hydrogel layer B in buffers with pH 4 (10 mM acetate buffer, refractive index of $n_b = 1.3344$) and pH 7.4 (10 mM phosphate buffer saline, refractive index of $n_b = 1.3349$), see Fig. 4. We observed a higher thickness and a lower refractive index at the pH 7.4 ($d_h = 790 \text{ nm}$ and $n_h = 1.3490$) than at the pH 4.0 ($d_h = 611 \text{ nm}$ and $n_h = 1.3534$) which is probably caused by repulsive forces between the carboxy groups within the hydrogel film which are negative charged at higher pH.

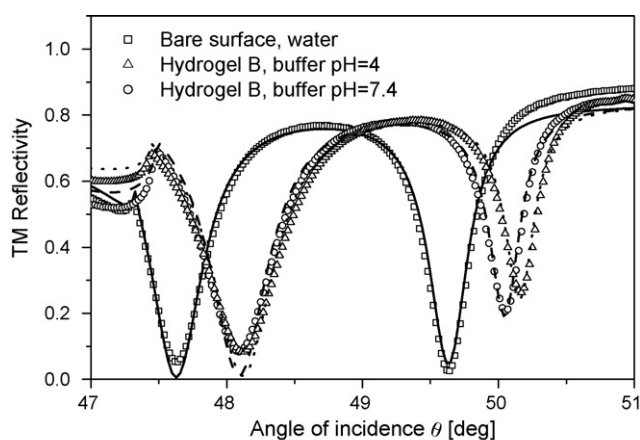


Fig. 4. Measured angular reflectivity spectra for the swelling of the hydrogel layer B in a buffer with pH 4 (triangle) and pH 7.4 (circle) compared to the spectrum measured for a bare gold surface (square) in contact with water. Fitted reflectivity spectra are shown for each sample (lines).

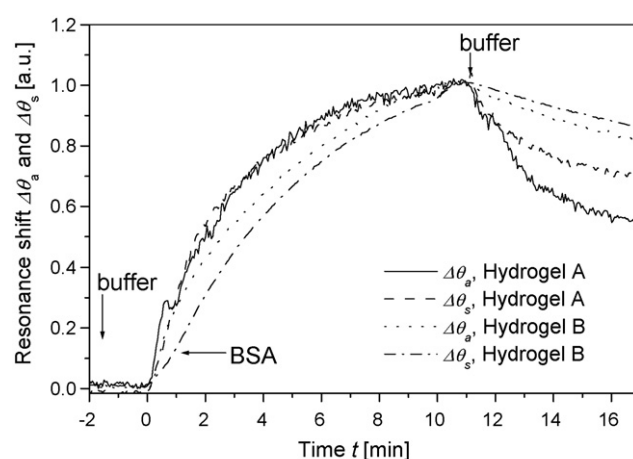


Fig. 5. Time evolution of $\Delta\theta_a$ and $\Delta\theta_s$ measured for the diffusion of BSA molecules into the hydrogel A cross linked for 15 min (solid line – $\Delta\theta_a$, dashed line – $\Delta\theta_s$) and hydrogel B cross linked for 40 min (dotted line – $\Delta\theta_a$, dash-dotted line – $\Delta\theta_s$). BSA dissolved in 10 mM acetate buffer with pH 5.5 at the concentration of 2.5 mg mL^{-1} .

Afterwards, we explored the diffusion of a bovine serum albumin (BSA) protein dissolved in a 10 mM acetate buffer with pH 5.5 into the hydrogels A and B. We measured the time evolution of changes in the resonant angles of incidence $\Delta\theta_a(t)$ and $\Delta\theta_s(t)$ upon the diffusion of BSA molecules into these hydrogels, see Fig. 5. Firstly, we rinsed the sensor surface with pure buffer for 2 min in order to establish a baseline. After, a solution with BSA (at a concentration of 2.5 mg mL^{-1}) was flowed through the flow-cell for 10 min. Finally, the sensor surface was rinsed with the pure buffer for 7 min. The measured time evolutions in Fig. 5 show that θ_a and θ_s are shifted towards higher angles of incidence upon the diffusion of BSA into a hydrogel due to the increasing of its refractive index n_h . The refractive index increase of $\delta n_h = 1.8 \times 10^{-3}$ and 3.6×10^{-3} was observed for the hydrogel A and B, respectively. These data reveal that the denser hydrogel was capable to uptake larger amount of BSA from a solution with pH 5.5. The diffusion of BSA to the hydrogel was probably driven by ionic interaction as no uptake of BSA was observed at pH 4 and 7.4.

Furthermore, Fig. 5 shows that the sensor response approaches faster the equilibrium for the hydrogel A than for the hydrogel B indicating that the diffusion is slower in a denser gel. In addition, one can see that the initial slope of the sensor response ($d\theta/dt$) measured for the angle θ_a is higher than that for θ_s . The reason for this observation is that the field of a-cLRSP excited at the angle θ_a penetrates deeper into the hydrogel film where BSA molecules diffuse faster from the solution. The s-cLRSP mode excited at the angle θ_s probes the region closer to the gold surface which is reached by diffusing BSA molecules in a later stage. We believe that simultaneous probing of thin hydrogel layers by cLRSP modes will enable future investigating of more complex structures (e.g. the diffusion through a hydrogel film with a gradient perpendicular to the surface) and determining important parameters (e.g. diffusion coefficient) through the analysis of kinetics $\Delta\theta_a(t)$ and $\Delta\theta_s(t)$ and their fitting with an appropriate model.

4. Conclusions

In conclusion, we described the implementation of new surface plasmon modes – cLRSPs – into a SPR sensor. These modes were excited by using a refractive index symmetrical layer structure with two thin metallic films. cLRSPs were used to simultaneously probe the sensor surface by their evanescent fields which exhibit different penetration depths into the sensed medium on its top. This feature

enabled the measurement of the distribution of refractive index changes perpendicular to the sensor surface which is not possible with conventional SPR sensors. We demonstrated the potential of cLRSP-based sensors in an experiment in which we investigated the swelling of thin hydrogel films on the sensor surface and the diffusion of protein molecules into these gels.

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Biographies

Jakub Dostálek received his PhD degree in physics from Charles University in Prague (Czech Republic) and since 2007 he is a project leader at the Max-Planck Institute for Polymer Research in Mainz (Germany). He was working as a research assistant at the Institute of Photonics and Electronics in Prague (Czech Republic) from 2000 to 2006 and he stayed as a postdoctoral fellow at the Max-Planck Institute for Polymer Research in Mainz (Germany) from 2006 to 2007. His research interests include guided-wave optics, plasmonics, fluorescence spectroscopy and optical sensors and biosensors.

Robert Fokko Roskamp received his diploma degree in chemistry from the Gutenberg University in Mainz (Germany) in 2006 and is now a doctoral candidate at the same university. He is researching the synthesis of functional hydrogels, their characterization and applications at the Max-Planck-Institute for Polymer Research in Mainz (Germany).

Wolfgang Knoll is head of Material Science department of the Max Planck Institute for Polymer Research in Mainz (Germany). He is also consulting professor at Stanford University (USA), visiting principal scientist at the Institute of Materials Research and Engineering (Singapore) and visiting professor at the School of Physics and Astronomy at Leeds University (United Kingdom). His current research interests include aspects of the structure/order–property/function relationships of polymeric/organic systems, in particular, in thin films and at functionalized surfaces. Strong emphasis is put on optical techniques to elucidate the structural and functional properties of supramolecular assemblies and nano-materials.