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Application of the photoluminescent ZnO thin layers in optical immunosensors. Original optical effects

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ZnO-based nanostructured thin films are broadly applied as a template for biosensors due to their fundamental physico-chemical properties. Optical properties of ZnO thin layers, in particular, an intense room temperature photoluminescence open a great possibility to be used for optical biosensor, in particular, immunosensor applications. Due to the progress in nanotechnology, the new methods have been developed for fabrication of nanostructured ZnO thin films with high surface area and advanced properties for biosensors, e.g. atomic layer deposition (ALD), metal organic chemical vapor deposition (MOCVD) and some others. In this report, the influence of the immobilized proteins of an immune complex on the photoluminescence spectra of ZnO thin films formed by ALD method and ZnO thin films consisted of vertically oriented ZnO nanorods grown by MOCVD is presented and discussed. Original optical effects observed during research, in particular, the appearance of resonant standing waves (Whispering Gallery modes) on the photoluminescence spectra and their immunosensor application are demonstrated.

Keywords: nanostructured ZnO, photoluminescence, immunosensor, thin films, Whispering Gallery modes.

Застосування фотолюмінесцентних тонких шарів ZnO в оптичному імуносенсорах. Оригінальні оптичні ефекти. *Алла Терещенко*

Наноструктуровані тонкі плівки на основі ZnO широко застосовуються як основа для біосенсорів завдяки своїм фундаментальним фізико-хімічним властивостям. Оптичні властивості ZnO, зокрема інтенсивна фотолюмінесценція при кімнатній температурі, відкривають великі можливості для використання в оптичних біосенсорах, зокрема, імуносенсорах. Завдяки прогресу в нанотехнологіях, нові методи були розроблені для виготовлення наноструктурованих шарів ZnO з великою площею поверхні та вдосконаленими властивостями для біосенсорів, такі як атомно-шарове осадження (ALD), металоорганічне хімічне осадження з газової фази (MOCVD) та деякі інші. В цій роботі показано та обговорено вплив іммобілізованих білків імунного комплексу на спектри фотолюмінесценції тонких плівок ZnO, сформованих методом ALD, а також тонких плівок ZnO, що складаються з вертикально орієнтованих наностержнів ZnO, вирощених за допомогою методу MOCVD. Представлені оригінальні оптичні ефекти, що спостерігались під час досліджень, зокрема, поява резонансних стоячих хвиль на спектрах фотолюмінесценції та їх застосування в імуносенсорах.

1. Introduction

Nanostructured ZnO films are known as material with unique combination of optical, structural, electrical and adsorption properties, therefore ZnO nanomaterials are broadly applied in a range of sensors. ZnO is a direct wide band gap semiconductor (Eg ~3.37eV) that has a high isoelectric point complemented by high surface to volume ratio of its nanostructures. Such properties like chemical stability, good biocompatibility and affinity towards biomaterials promote the use of ZnO in biosensors

and immunosensors [1]. Another advantage of ZnO nanomaterial is its optical properties, in particular, an instance photoluminescence at room temperature that allow the use of ZnO thin films as a transducer in optical biosensors. Photoluminescence based biosensors allow detection of biological interaction without any additional labels, e.g. fluorescent dye or quantum dots, what makes the procedure much easier. Besides, the optical signals detect the molecular interaction contactless, i.e. without contamination and significant damage of the biosamples [2]. Optical detection methods based on photoluminescence, reflectance, absorbance, fluorescence etc. demonstrate simple, fast and accurate detection of the target analytes in biosensing, in particular, immunosensing [1,2].

Immunosensors are the class of biosensors based on the reaction between antibody and antigen by formation of an immune complex. The interaction between antigen-antibody couple is known as highly specific and selective one [3]. The main challenges in the development of immunosensors are: selection of the most selective biomolecules that able to form complex with analyte; proper immobilization of biological materials providing selective recognition of analyte; application of the most efficient analytical transduction system [2,3]. Immunosensors are bio-analytical devices dedicated for selective determination of biological targets, which are mainly based proteins of the immune complex [4], in particular case – Grapevine virus A-type proteins (GVA). Grapevine virus A-type (GVA) is a plant vitivirus that is the most regularly detected virus in grapevine that general decline in the health of infected plants. [5]. Though GVA was identified over 35 years ago but it is still common in vineyards worldwide having a negative economic impact on vineyard productivity [6]. Up to date the monitoring and determination of GVA are based on the study of its genome, genomic organization and replication mechanism. Detection methods of GVA are based on serological methods (i.e. ELISA) and nucleic acid based methods (variety of PCR-based approaches). These methods provide high sensitivity but they are time consuming, labor intensive and quite expensive. Therefore there is a need to develop new, rapid and simple biosensor that would be sensitive to for determination of GVA virus.

Atomic layer deposition (ALD) is a relatively innovative technique, which allows the deposition of ultrathin metal oxide films with controlled thickness, grain size, surface morphology and defect concentration [7]. The mentioned structural parameters make a strong impact on optical, electrical, mechanical and other properties [2,7]. Metal organic chemical vapor deposition (MOCVD) is a well-known method for the formation of metal oxide thin films (as itself) and also can be used for the growth of nanorods of different size, shape and orientation on the substrate [8] that can act as a resonator where resonance standing waves also known as Whispering Gallery modes (WGMs) can be excited [9].The use of WGMs as a biosensor signal can provide the excellent means of sensitive, inexpensive and label-free biomolecule detection [10]. For instance, WGMs based sensors have been applied in the biomedical field for detection of interleukins or cancer biomarkers [11,12], for determining binding kinetics parameters [13], monitoring therapy responses [14], drug development process and biopharmaceutical research [10]. To date, different WGMs resonators have been designed for detecting molecular interactions, including glass spheres [12,15], ring resonators [11,16] as well as the micro- and nanostructures with hexagonal cross-sections applied in photonic devices as optical resonators useful for laser-based optoelectronics [9,17] and biosensors [18,19].

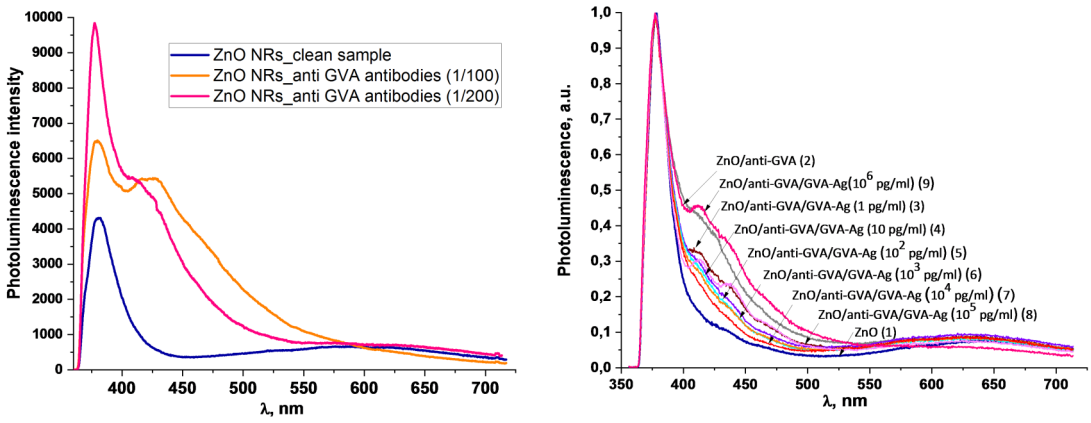
In this report, the photoluminescence properties of ZnO thin films, obtained by atomic layer deposition (ALD) and ZnO thin films contained vertically oriented ZnO nanorods (NRs) formed by metal organic chemical vapour deposition (MOCVD) were used as a biosensor signal for the determination of the GVA antigens proteins. An influence of the protein adsorption on photoluminescence properties of ZnO thin films is discussed.

2. Optical immunosensors based on ZnO thin films

2.1. ZnO thin films formed by ALD as a template of photoluminescence-based immunosensor. Functionalization of ZnO films

ZnO thin films formed by ALD were of wurtzite structure according to XRD results and the ZnO layers were of the thicknesses of 110 nm. The SEM images showed a conformal coating of the silicon substrates by ZnO films with a rough surface of the samples. The synthesis procedure and detailed characterization of structural and surface properties is described in previous work [20].

Optical properties of ZnO thin films were characterized by photoluminescence measurements using solid state laser with excitation wavelength of 355 nm and excitation power of 1.2 mW. The photoluminescence spectra of the ZnO films obtained by ALD were characterized by NBE peak at 378 nm and weak deep level emission (DLE) in the visible range (Fig 1a).



a) b)

Fig. 1. a) Photoluminescence spectra of ZnO thin film formed by ALD technique and ZnO thin film functionalized with anti-GVA antibodies using 1/100 and 1/200 diluted initial anti-GVA solution; b) dependence of the photoluminescence signal (normalized intensity) after incubation of ZnO-based immunosensing platform in different GVA-antigen concentrations containing specimens GVA-Ag.

The principle of the photoluminescence-based biosensor is based on the changes of the photoluminescence signal before and after immobilization of the biosensitive layer on the surface and after its interaction with the analyte [1-4]. The GVA proteins used in the experiment were provided by National Scientific Centre "Institute of Viticulture and Wine Making named after V. Ye. Tairov" (Odesa, Ukraine). The biosensitive layer was formed by the immobilization of anti-GVA antibodies on the surface of ZnO thin films. The anti-GVA antibodies were dissolved in the PBS with pH = 7.4 and further it was equally distributed on the surface of ZnO film with the size of 5×5 mm and incubated for 1 hour in humid environment at room temperature. After this, the samples were washed with PBS and then dried in air for 1 hour at room temperature. The same protocol was further used for GVA antigens specimen dilutions. The formation of biosensitive layer on the surface of ZnO resulted in the increasing of NBE peak intensity and appearance of a new photoluminescence band in the range from 400 to 550 nm (Fig. 1b). No NBE peak shift was observed. The optimal concentration of anti-GVA antibodies immobilized in the biosensitive layer was determined experimentally to be at 1/200 dilution of initial anti-GVA containing solution (Fig. 1a).

2.2. Immunosensor performance

The sensitivity of ZnO based immunosensor towards target analyte GVA-antigens was tested using the concentrations of GVA-antigen in the range from 1 pg/ml to 1 μg/ml. The interaction between immunosensing layer (ZnO/anti-GVA) and target analyte (GVA-antigens) resulted in the decrease of the NBE peak intensity for ZnO/anti-GVA/GVA-Ag based structures (Fig. 1b). However, the initial variation of the NBE peak intensity for all ZnO samples disabled the application of NBE intensity changes as a sensor signal. For this reason, the spectra were normalized. The response of the biosensor was based on the change in the intensity of the photoluminescence band at 425 nm corresponding to the protein related luminescence, caused by immobilized anti-GVA antibodies. The response of the as formed immunosensor was observed at the antigen concentrations from 1 pg/ml to 10 ng/ml, where the intensity of protein related photoluminescence band decreased with the increase of the antigen concentration (Fig. 1b). The further increase of the antigen concentrations led to the increasing photoluminescence intensity and further full saturation of the photoluminescence signal at the 1 μg/ml.

The biosensor response (S) was calculated using the equation:

$$S = (I_{Ab} - I_{Ab\text{-}Ag})/I_{Ab} \quad (1)$$

where: I_{Ab} is a photoluminescence intensity at 425 nm of ZnO with immobilized anti-GVA; I_{Ab-Ag} is the photoluminescence intensity at 425 nm of ZnO with immobilized anti-GVA antibodies and GVA-antigens.

The sensitivity of the obtained biosensor to the GVA antigen was in the range from 1 pg/ml to 10 ng/ml. The selectivity of the immunosensor was checked by the incubation of ZnO/anti-GVA-based structure with control specimen "Ag-", isolated from the non-infected grapevine plants and did not contain any GVA proteins. Such incubation resulted in the decrease of NBE peak intensity and photoluminescence emission in the region of 400-500 nm. However,

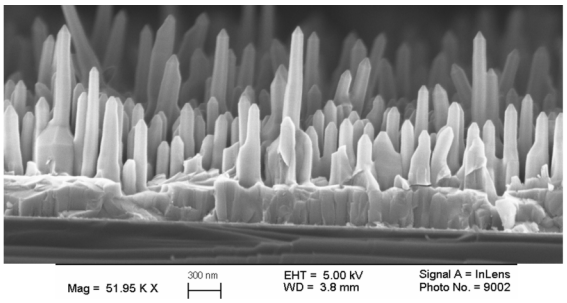


Fig. 2. SEM image of ZnO NRs grown on silicon substrates by method of atmosphere pressure metal organic chemical vapour deposition (APMOCVD).

unlike the case of GVA-Ag specimen, photoluminescence lines, related to the GVA emission, have overlapped with each other and intersected at wavelength around 425 nm. Therefore, no specific biosensor response was observed in the absence of GVA antigens [20].

2.3. ZnO NRs generating WGMs as a template of photoluminescence-based immunosensor

ZnO thin films grown on silicon substrates by method of atmosphere pressure metal organic chemical vapour deposition (APMOCVD) consisted of vertically oriented ZnO NRs, having the average dimensions of 200 nm in diameter and up to few micrometers in length. SEM image of vertically oriented ZnO nanorods is shown on figure 2. AFM investigation of the morphology of ZnO NRs has confirmed SEM-based observations. The average of root mean square (Rms) roughness calculated from AFM images was 35 nm. The XRD spectra confirmed the single phase ZnO of wurtzite structure. The detailed information of structural characterization of ZnO thin films can be found in earlier published work [8].

The photoluminescence spectra of ZnO NRs deposited by MOCVD were characterized by an intense near band edge (NBE) peak centered at 378 nm and by an extraordinary form of the photoluminescence emission in the visible range that was observed as defect-related photoluminescence of ZnO NRs (Fig. 3). Obviously, the optical resonance standing waves, known also as Whispering Gallery modes (WGMs), were generated inside the ZnO layer formed out of ZnO NRs that created a regularly shaped optical resonator, where WGMs can be excited [9].

This effect is induced by the morphology of the samples i.e. vertically grown ZnO NRs with rather uniform shape and orientation. The hexagonal structure of the vertically oriented ZnO NRs with particular incidence angle, creates optical WGMs resonator based on some ZnO NRs when the light is reflected from each facet and inside of the WGM resonator, that is determined by the incidence angle of ~20° vs the plane of the substrate on which ZnO NRs are formed. Such conditions of the photoluminescence measurements enable to observe the so called' quasi-WGMs' [21,22], when WGMs are generated by light-path inside of the hexagonal WGM resonator formed in ZnO NRs. An envelope curve of the WGM peaks in the visible range forms a defect-related (deep level) photoluminescence emission of ZnO NRs deposited by APMOCVD, centered at around 525 nm, similarly to the results described in other studies [1].

In the most of the crystal structures quasi-WGMs are hardly observable due to the low quality factor (Q) and therefore they are not frequently investigated. Hence, here presented results, which demonstrate that even the ZnO NRs of such small diameter (200 nm) can serve as a WGM resonator where quasi-WGMs can be excited, have a significant scientific value. In this case, the quality factor (Q), calculated according to the formula (2), is 27 for WGMs presented on the spectrum on the figure 3. By these results it is demonstrated that ZnO NRs is an additional type of WGM resonator that can be used for WGMs excitation.

$$Q = \frac{\omega_0}{\gamma_0} \qquad (2),$$

where Q – quality factor, ω_0 – resonance frequency, γ_0 – full width at half maximum of the mode.

The intensity of the NBE peak of the samples 20000 to 40000 a.u. that caused by an increase of ZnO NRs layer thickness along the silicon substrate. The latter can be caused by the distribution of diameter of ZnO NRs formed on the silicon substrate and due to the fact that the morphology and size of an WGM resonator greatly affect the energy and resonance levels of the resonant modes [17-19,23].

The basic principle of WGMs-based optical sensors relies on the entrapment of light inside a circular resonator, which acts as an optical cavity. Due to resonance conditions only the so called WGMs are allowed and detected as narrow peaks in the optical spectrum [24,25]. Any modification on the surrounding environment of the resonator (e.g., binding of biomolecules) induces a shift in the WGM wavelength position that is correlated to the total mass of bound molecules [10].

The functionalization procedure and conditions of the photoluminescence measurements of the ZnO thin films consisted of NRs was similar to the one described for ZnO thin films formed by ALD in the chapters 2.1 and 2.2. Thus, the photoluminescence spectrum of the ZnO NRs was completely different demon-

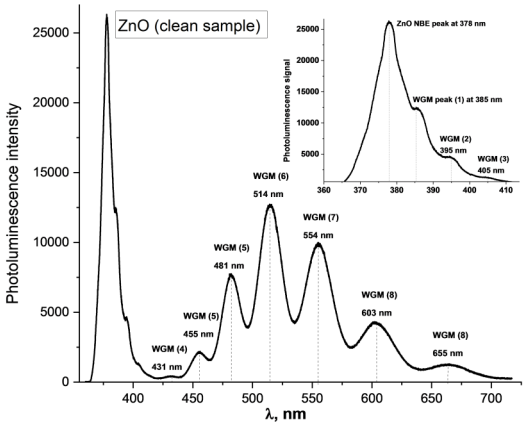


Figure 3. Photoluminescence spectrum of ZnO-NRs vertically oriented to the surface of silicon substrate with WGMs generated inside of optical resonators formed in the ZnO-NRs structure.

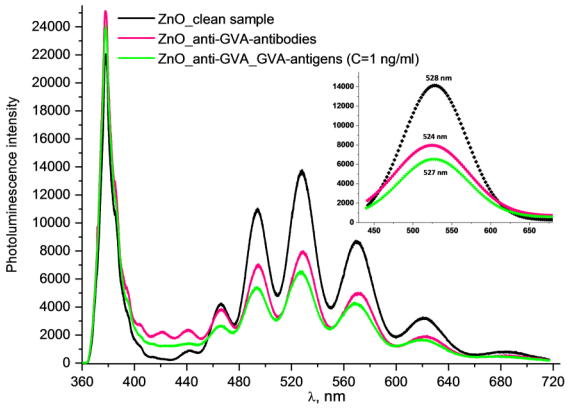


Figure 4. Photoluminescence spectra of ZnO NRs and ZnO-NRs/anti-GVA antibodies based structures incubated in aliquots containing 1 ng/ml GVA-antigen concentration; inset - the Gauss fittings of the envelope curves of WGMs peaks in the visible range of photoluminescence spectra.

strating the WGMs on the spectra (Fig. 4), such photoluminescence signal can be also used as a biosensor signal. An envelope curve of the WGM peaks in the visible range forms a defect-related (deep level) photoluminescence emission of ZnO NRs deposited by APMOCVD, centered at around 525 nm, similarly to the results described in other studies [26]. The Gaussian fitting of the envelope curve of the WGM peaks in the visible range indicates the maximum of photoluminescence emission at 528 nm (Fig. 4, inset), the standard error, which is indicated in the inset, is about 2.5 nm.

After the first test of immobilization of anti-GVA antibodies on the surface of ZnO NRs no changes in the photoluminescence signal were observed. The reason was that the surface of as grown ZnO NRs structures was determined to be very hydrophobic what enabled an effective immobilization of proteins by simple adsorption on ZnO NRs structures and it was not suitable for the design of an immuno-sensing platform. Therefore, in order to make the surface of ZnO NRs less hydrophobic, the samples were irradiated by UV illumination with excitation source of 255 nm during 30 min [27].

The immobilization of anti-GVA antibodies on the surface of the UV irradiated ZnO NRs of the initial anti-GVA sample diluted by 1/200 ratio resulted in several effects:

– an increase of the NBE peak intensity of ZnO NRs by 15 % in average, which has been typically observed in many researches [20,28];

– the appearance of a new photoluminescence band in the region from 400 to 450 nm, which is in line with the results reported in an earlier research [20];

– in the change of the position and intensity of WGMs peaks.

After immobilization of anti-GVA antibodies and after interaction of the formed immunosensing platform with GVA antigens the positions of each WGM peak changed non-equally, therefore the 'Gauss fitting curves' were plotted for each photoluminescence spectrum and are shown on the inset of figure 4. Immobilization of anti-GVA antibodies on the surface of ZnO NRs resulted in the UV-shift of defect related photoluminescence emission of 4 nm, 10 nm and 22 nm observed for different ZnO NRs samples. The ZnO NRs samples have demonstrated high reproducibility of the changes in photoluminescence signal, in particular, WGMs peaks positions and their intensity that have resulted after immobilization of anti-GVA antibodies on the surface of ZnO NRs (9 repetitions, 7 % error). Incubation of the ZnO-NRs based immunosensing platform in different concentrations of GVA-antigens, that were the target analyte which specifically binds to immobilized anti-GVA antibodies, resulted in some decrease of the NBE peak by 6% in average, which is typical for ZnO according to the other researches [20,21], and some IR shift of the WGMs peaks (Fig. 4). When the ZnO NRs/anti-GVA based immunosensing platform was incubated in solution containing low concentration (1 ng/ml) of GVA antigens the integral intensity and absolute amplitude of WGMs has decreased comparably to that of the ZnO NRs/anti-GVA (Fig. 4). When the formed immunosensing platform was incubated in solution containing higher concentrations of GVA-antigens, then the integral intensity of registered WGMs has increased, while the absolute WGMs amplitude remained almost the same. The Gauss fitting based approximations (Fig. 4, inset) demonstrate opposite changes in the defect-related photoluminescence band as a result of an interaction of anti-GVA antibodies immobilized on ZnO thin

film with GVA-antigens – backward shift of the 'Gauss fitting curves' towards IR region by 2.5 nm, 4.4 nm and 4.4 nm for ZnO-based immunosensing platforms incubated in solutions containing 1, 100 and 200 ng/ml concentrations of GVA-antigens, correspondently.

The formed ZnO NRs/anti-GVA immunosensor structure, which generates WGMs, shows the sensitivity towards GVA-antigens in a concentration range of 1-200 ng/ml.

Unlike the other sensors (e.g., fluorescent sensors), that usually require analyte labelling or modification, optical resonators detect analytes in their pristine (initial) form. This presents several advantages over label-based counterparts, such as faster analytics, possibility of real-time kinetic studies, and no alteration of bio-affinity due to the incorporated labels [29,30].

3. Analysis of the results (discussion)

The immobilization of GVA immune complex proteins on the surface of ZnO thin films resulted in the significant changes in the photoluminescence signal, i.e.an increase of NBE peak intensity, appearance of the new protein related photoluminescence band for both types of ZnO thin films, and the opposite shifts of defect related photoluminescence line for vertically oriented ZnO NRs that served as a resonator where WGMs were observed.

In the case of formation of the biosensitive layer by direct adsorption of anti-GVA antibodies the binding between ZnO and the biomolecules occurs due to Van der Waals forces, electrostatic interaction and hydrogen bonds [28]. The increase of the photoluminescence intensity of the NBE peak after the formation of the biosensitive layer can result from the charge transfer between anti-GVA molecules and the conductance band of ZnO [20, 28]. Quenching of the NBE ZnO peak and the decrease of the photoluminescence intensity related to anti-GVA antibodies (proteins) after their interaction with target-analyte (GVA antigens), may be induced by several reasons [20,26,28,31,32,33]:

– the surface reaction with a quencher may introduce non-radiative surface defects;

– charge transfer from a radiative material to a quencher;

– collisional photoluminescence quenching mechanism is responsible for the recognition of the analyte.

The appearance of the protein related luminescence band in the range of 400–500 nm can be caused by radiative transitions from defect states in the forbidden gap to valance band of ZnO. From the other side, the increase of photoluminescence peak at 425 nm observed at high concentrations of anti-GVA antibodies is in the same region as the blue emission peak of Zinc Sulfide (ZnS) [34,35]. This fact indicates that during the adsorption process the disulfide bonds formed between the chains of anti-GVA at least partly dissociate and forms strong complexes (-O-Zn-S-anti-GVA) with Zn atoms from the ZnO structure [20].

The obtained results demonstrate a high potential for the application of ZnO NRs in the design of immunosensors, where the analytical signal is determined by the assessment of a WGMs-based signal. Therefore, the future improvement of the ZnO NRs formation procedure in order to obtain more uniform structures with well-defined optical parameters will allow the development of highly sensitive immunosensors based on the WGMs excited within optical resonators in ZnO NRs-based layers.

4. Conclusions

The results presented in the given work indicate that photoluminescent properties of nanostructured ZnO films obtained by ALD and MOCVD techniques can be applied for determination of presence and concentration of bio-analytes, in particular, GVA-antigens. Considering the physical and chemical properties of ZnO thin films (i.e. high chemical stability, good biocompatibility, etc.) they have great prospects to be used as transducer material in optical biosensors, since its photoluminescence is easily excited and registered as a biosensor signal, and the interaction with proteins changes the optical properties of ZnO.

The obtained results demonstrate that the thin film based on hexagonal ZnO NRs of rather small diameter (200 nm), vertically oriented on the surface of silicon substrates, can serve as a WGMs resonator in which quasi-WGMs can be excited. The immobilization of anti-GVA antibodies on the surface of ZnO NRs-based layer resulted in a UV shift of the WGMs peaks in the visible range of spectra. Further interaction of the biologically selective layer with GVA-antigens resulted in the opposite shift of the WGMs peaks observed as a defect-related photoluminescence emission of ZnO NRs. The sensitivity of the immunosensor based on ZnO NRs vertically oriented on the silicon substrate obtained by MOCVD towards GVA antigens was in the range from 1 ng/ml to 200 ng/ml.

The sensitivity of the immunosensor based on ALD formed ZnO thin film to the GVA antigens was in the range from 1 pg/ml to 10 ng/ml. The detection of GVA antigens using optical properties of ZnO film formed by ALD method proved to be relatively sensitive and selective analytical approach, which could be charac-

terized as an express method, because it does not involve the application of additional labels, such as enzymes, which are used in ELISA or fluorescent-dyes, which are used in RT-PCR.

Due to good performance and simplicity of here described immunosensor ZnO-modified substrates can be applied as a platform for the development of other immunosensors based on immobilized antibodies, which would be sensitive to selected analyte.

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