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NANOAPERTURE ARRAY-BASED PLASMONIC SENSORS OF DANGEROUS SUBSTANCES USING TRANSPARENT CONDUCTIVE OXIDES

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Abstract: *Detection of dangerous substances like explosives, pathogenic microorganisms and toxic chemical is of utmost interest for homeland defense and anti-terrorist actions. Among the devices of choice for that purpose are surface plasmon resonance (SPR) chemical-biological sensors since they are ultra-fast, highly sensitive and label-free. We consider one of the advanced types of SPR sensors, those with ordered arrays of subwavelength apertures in plasmonic material. Such sensors show high sensitivity in transmission readout mode, are useful for both liquid and gaseous analytes and can be used as a building block for complex microfluidic systems for multianalyte detection. Simultaneously, high electromagnetic field concentrations in nanoapertures enhance nonlinear effects, thus further facilitating detection of complex molecules of dangerous substances. We performed finite element simulation of the performance of such devices for various materials and nanoaperture sizes and shapes. We dedicated special attention to the case when the subwavelength array is formed in transparent conductive oxide (TCO) host. An example of TCO is tin oxide, routinely used in thin layers for window defrosting and defogging elements in armored vehicles. We show that compared to conventional nanoaperture array sensors based on metal hosts the TCO-based devices simultaneously offer enhanced selectivity and retain high sensitivity.*

Key words: *plasmonic sensors, nanotechnologies, CBRNe agents, extraordinary optical transmission, transparent conductive oxides.*

1. INTRODUCTION

The detection of chemical, biological, radiological, nuclear and explosive (CBRNe) threats is of crucial importance for homeland defense and anti-terrorist actions [1, 2]. Facilities like airports, railway and metro stations, shopping malls and generally locations where many people are likely to gather are under great threat and possible chemical or explosive attacks could cause high mortality. It is thus necessary to unambiguously sense the presence and possibly detect the amount of dangerous substances and at the same time reduce the disruption of the routine of the present persons to the minimum.

The detection of usual hazardous materials, like those used in industry, is also of great importance, especially bearing in mind that many of such materials could be used as explosives or chemical agents for improvised terrorist devices with various degrees of sophistication [3]. One typical example of these is ammonium nitrate, readily available and routinely applied fertilizer that has also been used as potent explosive [4]. A further difficulty lies in the fact that dangerous substances may typically be enclosed in some kind of casing and hidden, so that the detection system must be able to recognize trace amounts of such chemicals [4]. An example are landmines that are buried underground and at the same time enclosed in their casings, so that only minute amounts of gases usable for recognition are released into the surrounding atmosphere [5].

It is desirable that the systems suitable for the detection of CBRNe agents be highly sensitive and highly selective, with small dimensions and weight (especially if needed for personal detection kits), simple to use and reliable. The basic part of all of such systems is the sensing element. There is a number of different sensors that are utilized in various situations, most of them based on the adsorption of the target analyte particles to the active surface of the device. Some of them include chemical field-effect transistors, electrochemical sensors, fluorescent sensors, microcantilever-based devices, etc. [6, 7].

Among the more recently introduced ones sensors for CBRNe detection are the surface plasmon resonance (SPR) devices [8-10]. They are extremely fast and sensitive, miniature, label-free, simple and robust. In their most basic form they simply consist of a slab of metal surrounded by an environment containing the target agent (obtained either by sampling the endangered area(s) or by simply placing the sensor at the location to be checked. An ultrathin layer of analyte (often monatomic or monomolecular) adsorbs at the slab surface. Alternatively, the whole sensor may be immersed into the analyte. In both cases this modifies the value of refractive index near the surface. The sensor readout is based on surface plasmon polariton (SPP) electromagnetic wave that is localized exactly at the interface plane, thus overlapping with the location of the adsorbed agent, and is evanescent in both perpendicular directions. Thus the SPP "sees" even the monolayer of agent as a strong perturbation of its propagation conditions. The consequence is that it is able to detect even changes equal to a few percent of a single monatomic layer [11].

More complex and more potent SPR sensors include various, usually periodic, combinations of metals and dielectrics, most often at the nanometer scale. Such artificial structures ensure enhanced sensitivity and selectivity and at the same time allow for simpler readout compared to the conventional SPR sensors. They are sometimes denoted as generalized SPR sensors based on plasmonic metamaterials [12-14].

An important type of generalized SPR sensors is a two-dimensional nanohole array in plasmonic material sheet [15, 16]. Such structures were first described within the context of extraordinary optical transmission effect [17]. The dimensions of the nanoapertures in the array are subwavelength, i.e. much smaller than the operating wavelength. The classical theory of Bethe as well as the common sense expect that no light can be transmitted through such a structure if the plasmonic part is optically opaque, since no polarization is allow to cross such a barrier [18, 19]. However, Ebessen et al [17] experimentally confirmed that in reality there is a transmittance peak of almost 100% through such structures – the effect being denoted as extraordinary optical transmission (EOT). Due to the possibility to integrate such arrays into microfluidic systems and to fill nanoapertures with the target agents, EOT arrays were proposed for chemical sensing application [15, 16]. Such sensors can be operated in transmission readout mode, are useful for both liquid and gaseous analytes and can be used in complex microfluidic systems for multianalyte detection.

Besides the most often used plasmonic materials like gold or silver, there are also alternative materials with lower losses and shifted values of the plasma frequency [20]. These include transparent conductive oxides (TCO) [21, 22] like indium oxide, tin oxide and zinc oxide. Their doped combinations include ITO (indium tin oxide) and AZO (aluminum zinc oxide).

Typical TCO plasma frequencies are in the near infrared and their absorption is lower than that in metals. The plasma frequency of TCO can be modified by doping [23]. TCOs themselves are well-known sensing materials, their conductivity being changed by the presence of analyte [24]. In spite of many benefits of the use of TCO for plasmonics, the applications utilizing these materials are very scarce. This is a consequence of the fact that they were recognized as low-loss alternative plasmonic materials only very recently.

There is a huge number of different agents to be detected in anti-terrorist actions. A prototype explosive agent, often used and often searched for is surely trinitrotoluene (TNT). Plasmonic sensors were utilized for the detection of trace amounts of this agent in a number of different situations [25-27].

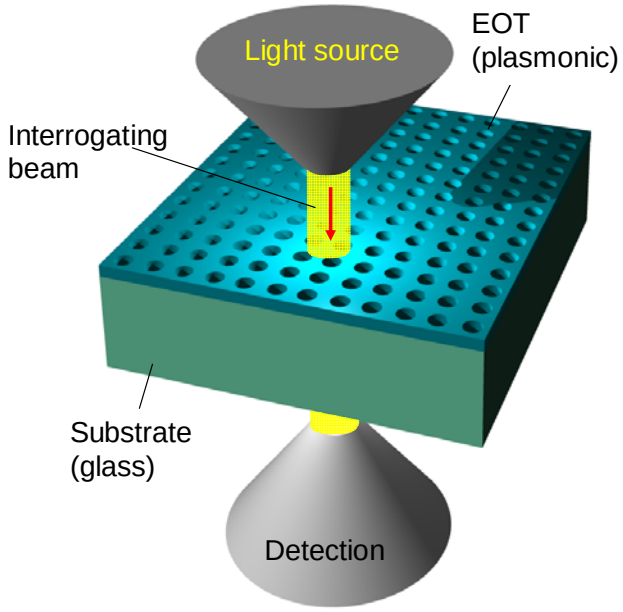
This paper investigates the properties of different nanoaperture-based plasmonic sensors, including those based on TCO, but not limited to them. We performed finite element simulation (FEM) of such devices for different materials and nanoaperture properties. As an example the case of SPR detection of trinitrotoluene (TNT) is considered.

2. PROBLEM DESCRIPTION

The sensing scheme utilizing an array of subwavelength holes in plasmonic material as a sensing element with tunable transmission is shown in Fig. 1. A white light source is utilized to illuminate the structure with an EOT array in plasmonic material. The nanohole array is situated in a chamber in which one may bring analyte liquid or gas.

A fiber is placed behind the nanohole array (denoted as "detection" in Picture 1) and its position can be adjusted utilizing an xyz micropositioner stage. The optical signal from the fiber is brought directly to a spectrophotometer

where the normal transmission is determined. In this simple setup each change of spectral transmission caused by the presence of the analyte is directly detected. The same setup could be used to measure oblique transmission as well.



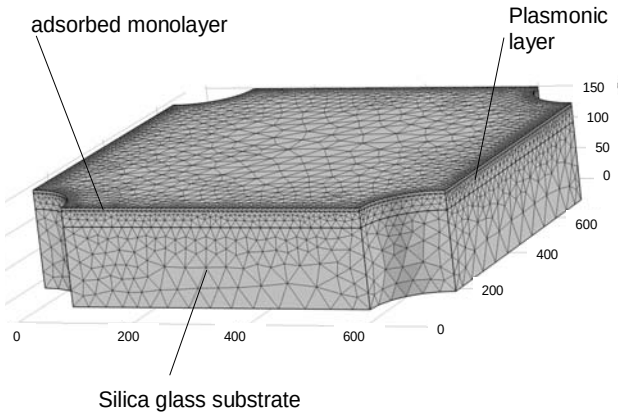
Picture 1. Setup for the use of a 2D extraordinary optical transmission array of nanoholes for transmission-based measurement of CBRNe agents (transmission mode)

The spectral transmission for different plasmonic materials under incidence perpendicular to the active surface was calculated utilizing finite element modeling (FEM). A single unit cell of the nanoaperture array with extraordinary optical transmission is shown in Picture 2. A layer of plasmonic material is deposited onto a glass substrate with a relative dielectric permittivity of 5.5 and with negligible absorption losses in the range of interest. A quarter of nanohole is seen in each corner of the structure. An analyte monolayer (thickness 0.3 nm) is formed on the plasmonic material.

3. NUMERICAL

In our simulations we utilized a full 3D finite element approach with tetrahedral elements. The COMSOL Multiphysics software package was utilized with the RF module. We applied an adaptive mesh approach, refining the mesh density near to the surfaces with the largest field gradients. Picture 2 shows the shape of the finite elements utilized to model the unit cell.

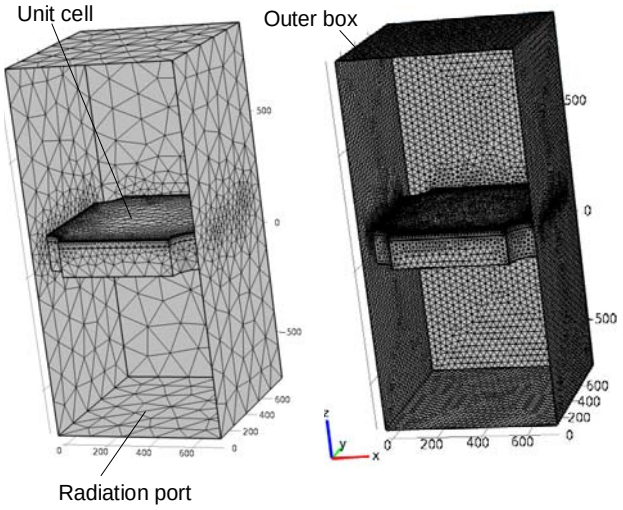
We utilized lumped elements and perpendicular irradiation (along z-axis). The starting side length of finite elements varied between 2 nm and 50 nm. A combination of perfect electric conductor (PEC) and perfect magnetic conductor (PMC) boundary conditions was used on the left/right and front/back sides, while the waveport for excitation (radiation port) was from the bottom side. The output were S-parameters, S_{11} and S_{21}, i.e. reflection and transmission coefficients.



Picture 2. Unit cell geometry. Plasmonic layer thickness is 25 nm, Silica glass thickness is 125 nm, width 710 nm, length 710 nm and hole radius 100 nm

For the sake of simplicity and to minimize the computation time, the analysis of the infinite structures was accomplished by taking into account a unit cell. Unit cells for simulations were constructed using structures with one radiation port at the bottom as shown in picture 4.

Drude model was used to describe the spectral dispersion of relative dielectric permittivity ε both in the case of metals (silver and gold) and transparent conductive oxides (tin oxide – SnO_2 and indium tin oxide – ITO).

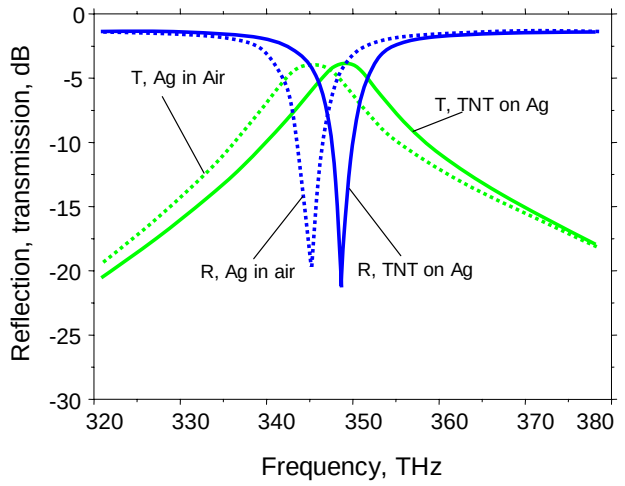


Picture 3. Unit cell geometry for S-parameters calculation with adaptable mesh geometry. Outer box with radiation port at the bottom in z direction is 760 nm width and length, height 1600 nm

4. RESULTS AND DISCUSSION

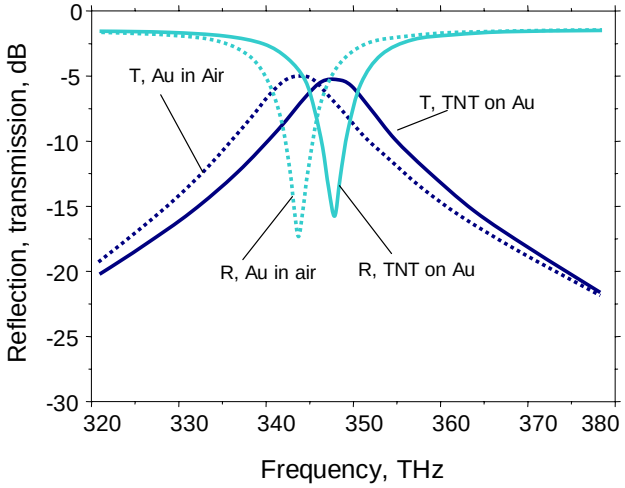
We performed our calculations of spectral transmission and reflection for silver, gold, tin oxide and ITO. The calculations were done for samples without an adsorbed layer and for those with a analyte layer consisting of TNT material. The dielectric permittivity of analyte with TNT was assumed to be 2.89 – *i* 0.072 [28].

Picture 4 shows the calculated spectral reflection and transmission of an EOT sample where the plasmonic material is silver.



Picture 4. Spectral transmission and reflection for silver-on-glass EOT structure with and without TNT adsorbed monolayer.

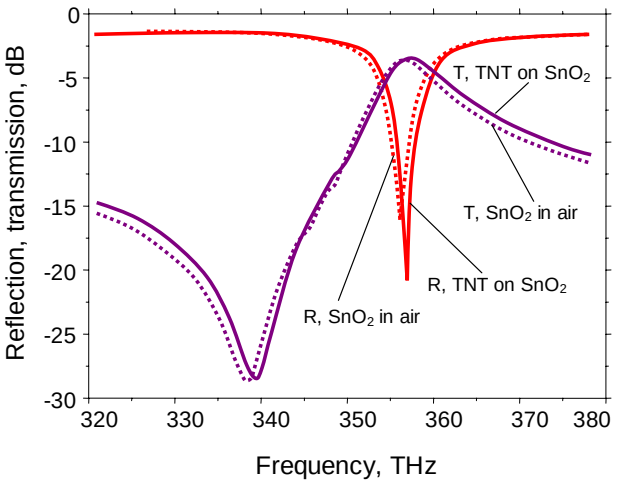
It can be seen that the transmission peaks are located between 345 THz and 350 THz. The presence of analyte shifts the transmission and reflection towards higher frequencies. It must be stressed that the calculation was performed for the case where only a single monolayer of explosive agent with an assumed thickness of 0.3 nm is adsorbed on the EOT sensor surface. Still, a significant and readily measurable frequency shift is observed.



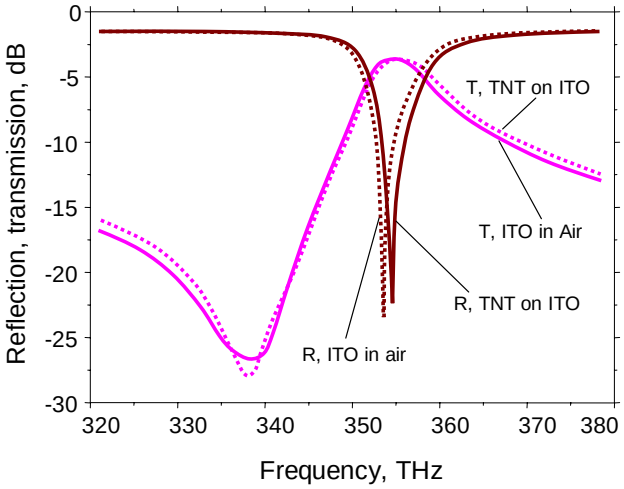
Picture 5. Spectral transmission and reflection for gold-on-glass EOT structure with and without TNT adsorbed monolayer.

Picture 5 shows the calculation results for the identical geometry, but the plasmonic material here is gold. Very similar results are obtained to those when Ag is utilized.

Next two pictures analyze the same geometry for the case when the active plasmonic constituent is transparent conductive oxide. For both SnO_2 and ITO we assumed the same electron concentration obtained through doping $n = 7.1 \cdot 10^{22}$ m^{-3}. Picture 6 shows the calculation results for the case when the plasmonic material is tin oxide (SnO_2 or TO). A shift of spectral characteristics is again observed here too. It is smaller than in the case of plasmonic metals, but still observable.



Picture 6. Spectral transmission and reflection for tin oxide (SnO_2)-on-glass EOT structure with and without TNT adsorbed monolayer.



Picture 7. Spectral transmission and reflection for indium tin oxide (ITO)-on-glass EOT structure with and without TNT adsorbed monolayer.

Finally, Picture 7 shows the simulation results when the active plasmonic material is ITO. The obtained spectral characteristics have a similar shape and comparable values.

One should stress here an important property of TCO generally (including both SnO_2 and ITO), it is the tunability of their resonance frequency. By choosing the dopant concentration, one is able to shift that frequency from near-infrared to ultraviolet range. This is actually one of the most useful features of TCO, since it ensures the possibility to choose the desired operating frequency range. In the above cases the situation with heavily n-doped TCO samples were considered, in order to obtain resonance frequencies in the range comparable to that of metals and thus ensure a direct and straightforward comparison of the two.

It is readily seen that the frequency shift due to the presence of explosive agent is smaller in the case of SnO_2 and ITO. The exact frequency of the peak, as mentioned above, is tunable by design. However, it is visible that the transmission change remains readily observable.

In spite of the fact that the transmission of the structure with SnO_2 is relatively large even if there are no EOT holes, the relative change of the transmission remains at least of the same order of magnitude in both analyzed cases. This shows that SnO_2 and ITO structures are also useful for EOT sensing. While the frequency shift is smaller than in the case of good metals, these materials ensure the possibility of engineering of their spectral response.

One should mention here that many TCO materials are very well known materials for chemical sensing themselves and that they react in the process of chemical absorption with different sensing materials. This makes it possible to utilize at the same time their plasmonic properties and their convenient behavior for chemical sensing.

5. CONCLUSION

We investigated the applicability of good metals like gold and silver and of transparent conductive oxides like tin oxide and indium tin oxide as alternative Drude-type plasmonic materials for sensing of chemical, biological, radiological, nuclear and explosive agents in trace amounts. To this purpose we analyzed a setup utilizing extraordinary transmission scheme with direct transmission readout. Our calculations show that the scheme offers a monolayer sensitivity to chemical and biological agents, comparable to other plasmonic sensors. An advantage of the investigated scheme is that it offers an additional degree of freedom over conventional readout schemes, as well as simplicity – no external couplers like Kretschmann prisms are necessary. A difference between the use of opaque metals and transparent conductive oxides is obviously that in the latter case overall transmission of the structure is larger. Thus the relative difference between transmissive and non-transmissive case, as tuned by the presence of CBRNe analyte, remains smaller. Counter-intuitively, the difference between the case with and without the target agent was comparable with the readout of the EOT structures with an opaque metal layer. On the other hand, the lower absorption of TCO in the present scheme allows for the use of alternative geometries. One such case are structures with in-plane propagation, where coupling is ensured by the existence of diffractive grating formed by the EOT nanoapertures.

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