Numerical analysis of a Kretschmann surface plasmon resonance sensor with silver/TiO_2/$BaTiO_3$/silver/graphene for refractive index sensing

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The sensitivity of a Kretschmann surface plasmon resonance (SPR) sensor was analyzed. The Kretschmann setup had multiple layers, a BK7 prism, silver, barium titanate ($BaTiO_3$), titanium dioxide (TiO_2), and graphene. The $BaTiO_3$ and TiO_2 coatings were sandwiched between two silver layers. The sensitivity of 260°/RIU has been achieved. The graphene layers are added to the configuration to improve sensitivity and as a bio-compatibility agent. This configuration can be used for biochemical sensors.

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Surface plasmon resonance (SPR) sensors have many applications in various fields of pathogens detection, medical diagnostics, and bio-markers analysis[1-3]. SPR sensors can characterize and detect biomolecules with high sensitivity. These SPR sensors monitor the changes in the refractive index at the metal-dielectric interface of the sensors. Minor changes in the refractive index change the resonance conditions and cause a shift in the recorded SPR signal[3-6].

SPR is a powerful tool for chemical and biomedical applications. The resonant energy coupling between the incident light and the metal-dielectric boundary plasmons is affected by the changes in the refractive index of the external environment. Surface plasmons are the coherent oscillations of free electrons on a two-media interface with opposite signs of dielectric permittivity. The surface plasmons have an electric field that peaks at the interface and then exponentially decays with distance. Surface plasmons require transverse magnetic (TM) light for excitation since the plasmons are TM[7]. Direct light cannot excite surface plasmons. The used incident light must have more momentum to achieve phase matching and excite the surface plasmons. To achieve momentum matching, prisms, fiber gratings, and waveguides can be used[8]. In the Kretschmann configuration, the light incident on the prism experiences attenuated total reflection (ATR), and an evanescent field forms on the thin metallic dielectric layer.

Silver, gold, aluminium, and copper have been used as plasmonic materials. Gold is useful due to its resistance to oxidization and corrosion[3]. However, gold can show low detection accuracy and wider resonance curves. Silver needs prior treatments to limit oxidization, but its narrow resonance curves are valuable in practice. With protective layers, sliver can be used more in SPR biosensors[2,9]. Plasmonic metals have poor adsorbability, and biomolecules show poor attachment to the metal interface of the sensor. Thus, two-dimensional (2D) materials can enhance the sensors' response to analytes.

Graphene is a common 2D material for enhancing SPR biosensor performance because of its charge carrier mobility and rich π conjugation structure. Due to its high surface-to-volume ratio, graphene can adsorb the analytes' biomolecule[1,9,10]. Graphene coatings can accommodate biological tissue samples and DNA/RNA. Graphene is a strong material with good flexibility, broadband absorption, and high transparency in the visible range of the spectrum. Graphene has been used in SPR sensors for frolic acid protein detection and showed a limit of detection of 5 fM[11]. Theoretical analysis showed that using ZnO with graphene on gold coated prism can achieve a sensitivity of 187.43°/RIU[9]. Anti-fouling coatings may be needed to ensure better performance for these sensors. However, 2D materials like graphene can cause unneeded energy loss due to their large extinction coefficient, resulting in wider SPR curves and shallower resonance dips.

Using metal oxide can improve SPR biosensors' sensitivity due to the enhanced intensity of the evanescent field. The titanium dioxide (TiO_2) has good chemical stability and a higher refractive index. Thus, it has been used to enhance SPR sensors' performance. A D-shaped

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fiber SPR sensor with gold/TiO_2 coatings was shown to have a theoretical maximum sensitivity of up to 30 000 nm/RIU[12]. The barium titanate ($BaTiO_3$) has a high refractive index and minimum loss with a 50%—70% porosity. The average pore size is 30 μm in diameter. $BaTiO_3$ was shown not to exhibit short-term toxicity, which can be useful for biosensing applications[13]. Theoretical work showed that the sensitivity of a Kretschmann setup with silver/$BaTiO_3$ could reach 257°/RIU[14].

$BaTiO_3$ and TiO_2 were used in this proposed sensor between two layers of silver to improve its sensitivity. The use of two layers of sliver showed better sensitivity when the $BaTiO_3$ and TiO_2 coatings were used. A graphene layer was used on the sensor to enhance its adsorption of biomolecules. Silver was used due to its sharp resonance dips as well. Numerical analysis using finite-difference-time-domain methods in a COMSOL platform was used to study the performance of the sensing structure.

The proposed sensor has six layers. The first layer is a BK7 prism. BK prism has limited dynamic range, yet they show good sensitivity and reflectivity. The dynamic range of a sensor is the range of refractive index changes that can be detected using angle interrogation[15-17]. The second layer is silver. The refractive index of silver can be obtained by Drude's model[18,19]. Silver was chosen due to its sharp resonance dips.

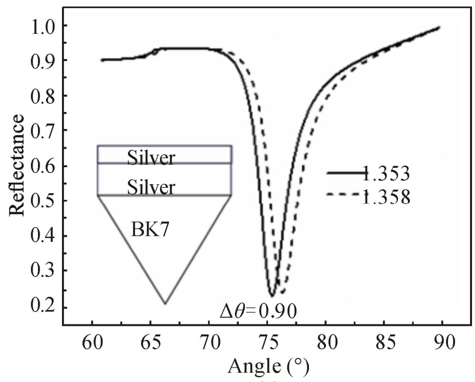
There were two different layers of silver used in this experiment. The first silver layer has a 50 nm thickness, and the second has a thickness of 10 nm. The refractive index of $BaTiO_3$ is 2.404 3 in the visible spectrum region. The thickness of the $BaTiO_3$ layer chosen here is 5 nm. The refractive index of the 2-nm-thick TiO_2 layer is 2.41. The last layer used is graphene, with a thickness of 0.34 nm per layer. The refractive index of the graphene is $3+ic/3\lambda$, with c=5.44 μm^{-1}[20,21]. The structure of the proposed sensor is shown in Fig.1. The simulation was conducted in COMSOL using a multilayer prism setup for angle interrogation.

The sensing principle of SPR sensors is based on the interaction of the intended analyte with sensing layers. The resultant refractive index change in the sensing medium causes a change in the resonance conditions of the plasmons. When the p-polarized monochromatic light reflects off the metal-dielectric surface of a prism, an evanescent wave is generated on that interface along the plasmonic metal layer propagating with the refractive index of the sensed analyte of 1.353—1.358. The sensitivity of the proposed sensor is $\Delta\theta/\Delta n$, which is the ratio of the total angle shift ($\Delta\theta$) divided and the difference in the refractive index Δn[9,15,22].

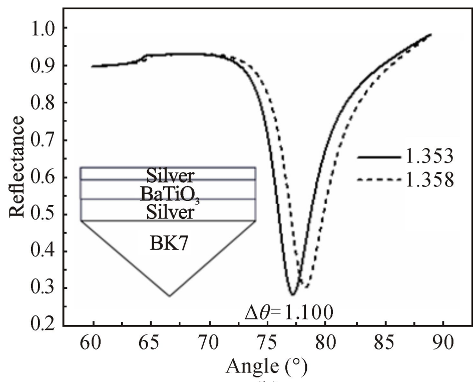
The aim of choosing the layers of the sensing system is to improve the sensitivity for biochemical sensing. Fig.2 shows the reflectance of the sensing systems as the analyte's refractive index varies within 1.353—1.358. The reflectance has a sharp dip at the resonance angle. As the $BaTiO_3$, TiO_2, and graphene layers are added, the shift in angle gets larger even though the refractive index remains the same. The total angle shift is 1.3° for the six-layer system.

The total angle shift was 0.9° when silver was used, as shown in Tab.1. A regular SPR sensor can be built by a prism, a plasmonic thin metal layer, and an analyte layer. However, the addition of graphene and $BaTiO_3$, and TiO_2 improves the sensitivity of the setup. The choice of additional materials and the order of layers improved the sensor's sensitivity.

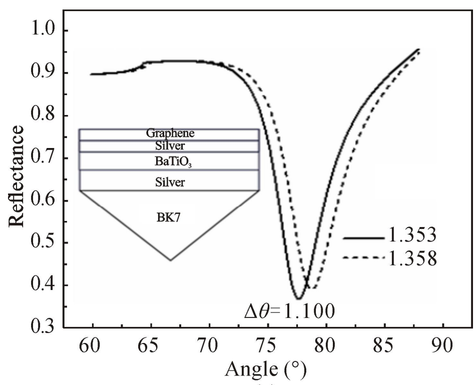
In Fig.2, the sensor's sensitivity was investigated as a function of the refractive index. The total angle of resonance shift was for the change in the refractive index of 1.330—1.360. The sensor in the Kretschmann configuration uses angular measurements. The changes in the refractive index cause a change in the refractive of the



(a)



(b)



(c)

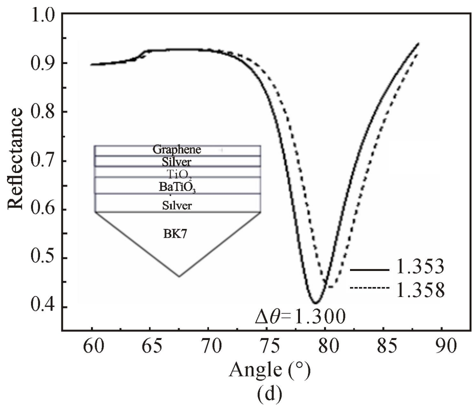


Fig.1 Reflectance versus angle of incidence with different layer configurations for (a) Ag/Ag, (b) Ag/$BaTiO_3$/Ag, (c) Ag/$BaTiO_3$/Ag/graphene, and (d) Ag/$BaTiO_3$/TiO_2/Ag/graphene

metal-dielectric surface. The subsequent change in the plasmon's wave vector plasmons changes the angle at which the incident light coincides with the wave vector of the plasmons. This angular shift is used to detect the presence of the analyte. Fig.2 shows that the sensitivity of the six-layer system increases until it reaches 260 at the refractive index range within 1.355—1.358. The sensitivity at the refractive index range of 1.333 is 200. As the refractive index of the analyte increases, the sensitivity increases.

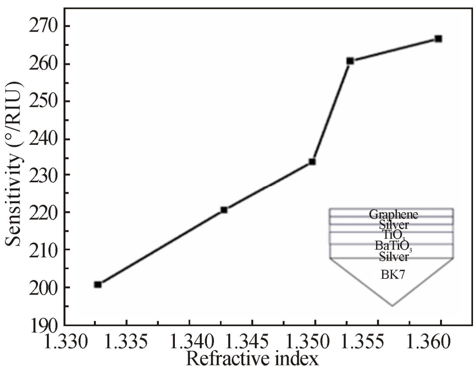


Fig.2 Variation of sensitivity with respect to analyte refractive index

Tab.1 Sensitivity of the sensor with different layer configurations at refractive index of 1.353 and 1.358

Fig.1	Layer	Angle shift (°)	Sensitivity (°/RIU)
(a)	Ag/Ag	0.9	180
(b)	Ag/$BaTiO_3$/Ag	1.0	200
(c)	Ag/$BaTiO_3$/Ag/graphene	1.1	220
(d)	Ag/$BaTiO_3$/TiO_2/Ag/graphene	1.3	260

Fig.3 shows the effect of the graphene layers. More graphene layers result in higher minimum reflectivity and full width at half maximum. The increases are due to increased energy confinement in these added layers. The graphene layers are needed for their biocompatibility for biochemical sensing. In experimental setups, care must be taken to limit the number of graphene layers used to avoid the effects of energy confinement.

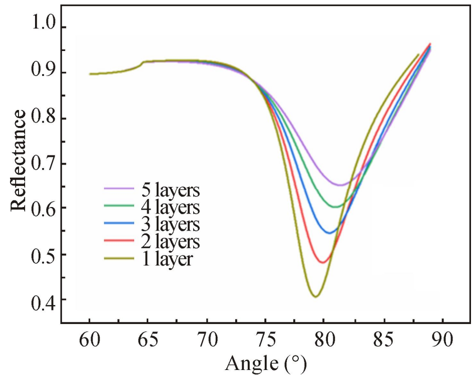


Fig.3 Reflectance versus angle of incidence with different graphene layers at wavelength of 633 nm

Electric field distribution is shown in Fig.4. The application of the sensing layers affects the electric field at the metal-dielectric interface. The electric field is increased by inserting those layers. The field reaches up to 105 at the analyte interface. This enhancement is due to the oscillation of the free electrons in Refs.[23] and [24].

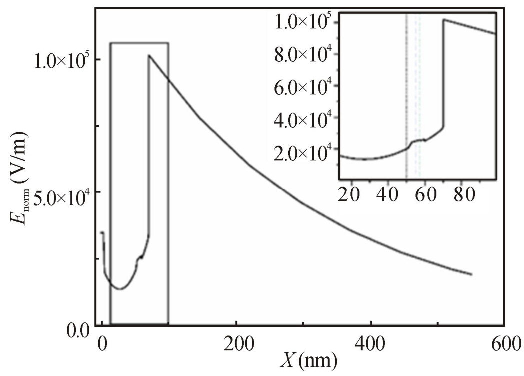


Fig.4 Electric field distribution at resonance angle of SP wave in the proposed sensor at wavelength of 633 nm (Inset: zoomed section of the electric field)

In this letter, an SPR sensor was developed to detect refractive index changes using silver graphene, $BaTiO_3$, and TiO_2. A Kretschmann configuration with angular interrogation was numerically analyzed. The sensor showed a shifting resonance dip with an increasing refractive index and sensitivity of 260°. The addition of graphene layers caused an increase in minimum reflectivity.

Ethics declarations

Conflicts of interest

The authors declare no conflict of interest.

References

[1] HAN L, DING H, LANDRY N N A, et al. Highly sensitive SPR sensor based on Ag-ITO-blueP/TMDCs-graphene heterostructure[J]. Plasmonics, 2020, 15(5): 1489-1498.

[2] LAMBERT A S, VALIULIS S N, MALINICK A S, et al. Plasmonic biosensing with aluminum thin films under the Kretschmann configuration[J]. Analytical chemistry, 2020, 92(13): 8654-8659.

[3] PATIL P O, PANDEY G R, PATIL A G, et al. Graphene-based nanocomposites for sensitivity enhancement of surface plasmon resonance sensor for biological and chemical sensing: a review[J]. Biosens bioelectron, 2019, 139: 111324.

[4] TIAN M, HUANG Y, LI C, et al. High-performance humidity sensor based on a micro-nano fiber Bragg grating coated with graphene oxide[J]. Optics express, 2020, 28(18): 26395-26406.

[5] FIRDOUS S, ANWAR S, RAFYA R. Development of surface plasmon resonance (SPR) biosensors for use in the diagnostics of malignant and infectious diseases[J]. Laser physics letters, 2018, 15(6).

[6] SINGH P. SPR biosensors: historical perspectives and current challenges[J]. Sensors and actuators B: chemical, 2016, 229: 110-130.

[7] DAS C M, GUO Y, KANG L, et al. Investigation of plasmonic detection of human respiratory virus[J]. Advanced theory and simulations, 2020: 2000074.

[8] HOMOLA J. Electromagnetic theory of surface plasmons[J]. Surface plasmon resonance based sensors, 2006: 3-44.

[9] KUMAR A, YADAV A K, KUSHWAHA A S, et al. A comparative study among WS_2, MoS_2 and graphene based surface plasmon resonance (SPR) sensor[J]. Sensors and actuators reports, 2020, 2(1).

[10] MENON P S, JAMIL N A, MEI G S, et al. Multilayer CVD-graphene and MoS_2 ethanol sensing and characterization using Kretschmann-based SPR[J]. IEEE journal of the electron devices society, 2020, 8: 1227-1235.

[11] HE L, PAGNEUX Q, LARROULET I, et al. Label-free femtomolar cancer biomarker detection in human serum using graphene-coated surface plasmon resonance chips[J]. Biosensors and bioelectronics, 2017, 89: 606-611.

[12] GANGWAR R K, AMORIM V A, MARQUES P V S. High performance titanium oxide coated D-shaped optical fiber plasmonic sensor[J]. IEEE sensors journal, 2019, 19(20): 9244-9248.

[13] BALL J P, MOUND B A, NINO J C, et al. Biocompatible evaluation of barium titanate foamed ceramic structures for orthopedic applications[J]. Journal of biomedical materials research part A, 2014, 102(7): 2089-2095.

[14] SUN P, WANG M, LIU L, et al. Sensitivity enhancement of surface plasmon resonance biosensor based on graphene and barium titanate layers[J]. Applied surface science, 2019, 475: 342-347.

[15] ROH S, CHUNG T, LEE B. Overview of the characteristics of micro- and nano-structured surface plasmon resonance sensors[J]. Sensors (Basel), 2011, 11(2): 1565-1588.

[16] SHARMA N K, YADAV S, SAJAL V. Theoretical analysis of highly sensitive prism based surface plasmon resonance sensor with indium tin oxide[J]. Optics communications, 2014, 318: 74-78.

[17] BRAHMACHARI K, RAY M. Effect of prism material on design of surface plasmon resonance sensor by admittance loci method[J]. Frontiers of optoelectronics, 2013, 6(2): 185-193.

[18] PRABOWO B A, PURWIDYANTRI A, LIU K C. Surface plasmon resonance optical sensor: a review on light source technology[J]. Biosensors (Basel), 2018, 8(3): 80.

[19] NGUYEN H H, PARK J, KANG S, et al. Surface plasmon resonance: a versatile technique for biosensor applications[J]. Sensors (Basel, Switzerland), 2015, 15(5): 10481-10510.

[20] CAI H, SHAN S, WANG X. High sensitivity surface plasmon resonance sensor based on periodic multilayer thin films[J]. Nanomaterials, 2021, 11(12): 3399.

[21] PAL A, JHA A. A theoretical analysis on sensitivity improvement of an SPR refractive index sensor with graphene and barium titanate nanosheets[J]. Optik, 2021, 231: 166378.

[22] UDDIN S M A, CHOWDHURY S S, KABIR E. Numerical analysis of a highly sensitive surface plasmon resonance sensor for SARS-CoV-2 detection[J]. Plasmonics, 2021: 1-13.

[23] YAO Q, REN G, XU K, et al. 2D plasmonic tungsten oxide enabled ultrasensitive fiber optics gas sensor[J]. Advanced optical materials, 2019, 7(24).

[24] DE OLIVEIRA H J B, MARTINS FILHO J F, DO NASCIMENTO J F. Computational modeling of H2S gas sensor using surface plasmon resonance in a D-shaped optical fiber[J]. 2018 SBFoton International Optics and Photonics Conference (SBFoton IOPC), October 8-10, 2018, Campinas, Brazil. New York: IEEE, 18403526.