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Self-Sensing Surface Plasmon Resonance for the Detection of Metallic Nanoparticles

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ABSTRACT

Surface plasmon resonance (SPR) is an established technique for label free sensing of bio-molecular species, including time-dependent reaction analysis. Unlike previous research by other workers, who have used gold or silver nanoparticles to enhance sensitivity by inducing LSPR, this study involves the theoretical development of a Localised SPR (LSPR) system where a glass prism is considered with multilayer films to enable the detection of metallic nanoparticles. Silver nanoparticles with a volume concentration 0.25 % can be clearly detected from both amplitude and phase, according to the results of these simulations. The model presented is rigorous in that it accounts for the effect of the Cr or Ti adhesion layers together with a graphene layer at the metal-sensing interface. This enables the direct detection of the presence of nanoparticles from their plasmonic amplitude and phase (self-sensing). Our model also demonstrates that the sensitivity of the sensors can be significantly improved with the introduction of graphene layers.

Keywords: Surface Plasmon Resonance, Graphene, Biosensor, Nanoparticles, Toxicology

1. INTRODUCTION

Since the pioneering experiments of Otto, Kretschmann and Raether in the late 60s to excite Plasmon waves on metal films [1], surface plasmon resonance (SPR) has become an established tool for biosensing, such as DNA-protein, protein-protein, protein-drug interactions; electrochemical analysis and molecular detection [2]. However, research into the application of nanoparticle detection using SPR [3] is relatively new. The SPR response has been enhanced by gold nanoparticles by adding a metallic plasmonic layer at the sensor interface. SPR measurements of biomolecular interactions on the surface of gold thin films have emerged as one of the leading techniques for fast in-situ detection of a wide range of biological targets. Over the past few decades SPR sensing technology has established a reputation for the detection of chemical and biological analytes along with medical diagnostics and environmental monitoring [4, 5].

Kwon *et al* [6] have used bio-functionalised nanoparticles of various shapes and sizes to enhance SPR for the detection of protein biomarkers at attomolar (aM) concentration levels. Using three different gold nanoparticle shapes (cubic cages, rods and quasi-spherical) with at least one dimension in the 40–50 nm range, each nanoparticle (NP) was covalently functionalized with an antibody (anti-thrombin) and used as part of a sandwich assay in conjunction with a gold SPR chip modified with a DNA-aptamer probe specific to thrombin. The enhancement in sensitivity enabled the detection of thrombin at concentrations as low as 1 aM.

In the Otto configuration a prism is placed above a gold thin film separated by a small air gap as shown in Figure (1, a). In this configuration the evanescent wave is coupled through the air gap into gold film. The evanescent wave becomes weaker as it decays exponentially away from the surface producing a mismatch of momentum between photons and plasmons making it difficult to excite

plasmons. Otto, Kretschmann and Raether [1] devised a similar experimental system, in the same year, where there was no gap between the prism and the thin metallic film, as shown in Figure (1, b) and the multi-layered system is presented in Figure (1, c) as well. In these cases it was found that a surface plasmon could be efficiently generated. This propagation matching of constants [7], known as resonance condition is given as:

$$\frac{2\pi}{\lambda_1} n_1 \sin \theta_{SPR} = Re \left[\frac{2\pi}{\lambda_1} \left(\frac{\epsilon_m - n_N^2}{\epsilon_m + \epsilon_N} \right)^{1/2} \right] \quad (1)$$

where θ_{SPR} is the resonance incident angle, n_1 , ϵ_m and n_N are refractive index of prism, dielectric constant of metal and the refractive index of sensing medium, respectively.

The experimental difficulty of positioning and sustaining, a very small gap between the metal film and the prism, ultimately meant that the Otto configuration did not gain much popularity, and modern day SPR experiments are based on the Kretschmann configuration [8]. It should be mentioned that today the Kretschmann configuration is utilized in both research [9] and commercial applications, such as the long established Biacore 3000 system [10].

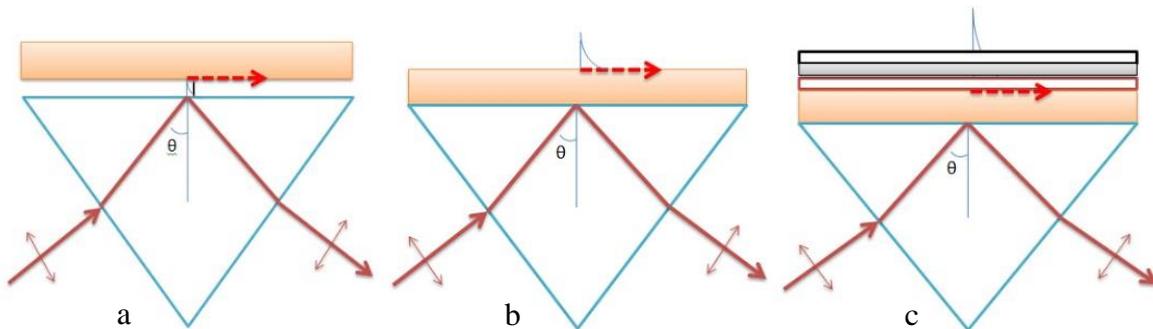


Figure 1 a) Otto configuration, b) Kretschmann configuration and c) multi-layered system. The incident light (P-polarised) undergoes total reflection at the prism base where evanescent waves are generated (dotted arrow) to propagate along the metal-prism interface.

Light from an LED or laser diode passes through the prism and is incident at the prism-film interface at an angle greater than the critical angle, θ_c . Although the far field light is reflected fully, a near-field electric field component is coupled into the metallic film [11, 12]. This is known as an evanescent wave – a wave which propagates along the metal-dielectric interface, yet decays exponentially in the orthogonal direction.

As the extent of energy transfer is ultrasensitive to the coupling conditions the refractive index of dielectric layer can be accurately determined by monitoring the reflected light intensity or phase. This occurs at a unique angle, characterised by a significant minima in the reflected beam, and a 180° phase shift, this is shown in Figure (2). The extreme sensitivity to refractive index / permittivity changes at the interface forms the basis for SPR sensing. It is important to note that, SPR can be used to detect precisely any changes in the refractive index or thickness of the surface films. This is because it is highly sensitive to the optical properties in the vicinity of the interface between a metal and dielectric. They are mainly divided into two categories, Propagating Surface Plasmons (PSPs) and Localized Surface Plasmons (LSPs). In a paper by Shankaran, Goby and Miura [13] the use of SPR immunosensors for biomedical and environmental applications was reviewed. The use of functionalised surfaces on top of the gold thin film enables bio-event to be measured. This functional technology can be applied to enzymes [14] antibodies [15], peptides [16] and DNA [17].

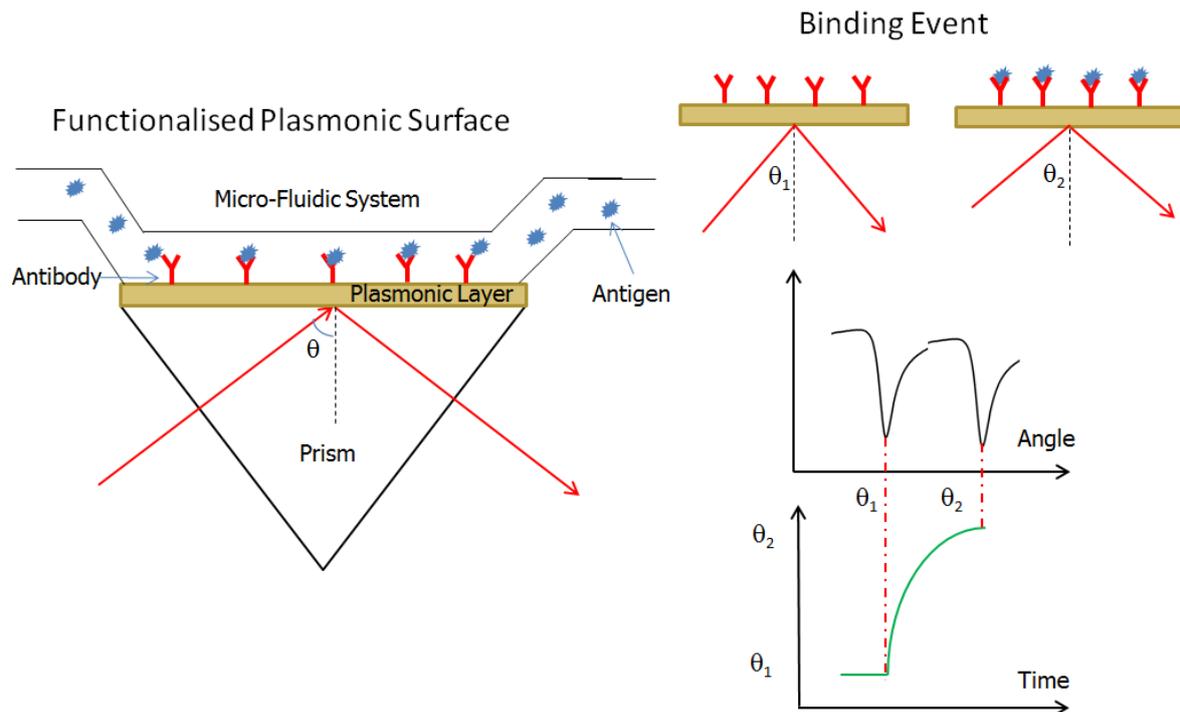


Figure 2 Schematic view of the surface plasmon resonance immunoassay technique. Functionalised SPR sensor layer on top of a conventional glass prism/ gold plasmonic system (left). The right side shows the sensogram response changing following binding event.

LSPs require metallic nano-particles in which they can be excited [18]. Therefore, a strong enhancement of electromagnetic field in the near-field region can be induced which results in their wide application in Surface-Enhanced Raman Scattering [19], fluorescence enhancement [20] refractive index sensitivity [21], and bio molecular interaction analysis [22]. In 2010 Bingham et al [23] used localized surface plasmon resonance to detect the presence of He, N₂ and Ar, which formed the local sensing environment, along with Ag and Au nanoparticles which support LSPR. In this work they were able to detect extremely small bulk refractive index changes of the order of 3×10^{-4} when sensing He, N₂ and Ar. LSPR was also able to detect the presence of water vapour in air at 40% humidity, compared to dry N₂. Kreno et al [24] used silver nanoparticles to detect similar bulk refractive index changes (5×10^{-4}). By growing a metal-organic framework on top of the nanoparticles the LSPR signal was enhanced 14-fold when detecting the presence of CO₂. Research at Plymouth University is focused on the detection of nanoparticles in aquatic environments; silver is the second most toxic element after mercury and is widely used in nanoparticle form suggesting that it is likely to enter rivers and estuaries; titanium dioxide is also very common in sun lotions and cosmetics and is very harmful to fish; as are carbon 'bucky balls' or fullerenes which can be found in anti-ageing lotions and creams.

2. SIMULATION OF SURFACE PLASMON RESONANCE

It is possible to predict the sensor response and calculate the change in refractive index of the sensed layer by using a mathematical model, which is based upon transfer matrix method [25]. The method can be easily extended for multi-layered system, which is of particular interest here. In the case of isotropic and homogeneous materials the wave propagation can be described by p- and s- polarised modes, so the characteristic matrix is of rank 2. Suppose that p-polarised light strikes the system from the first medium with refractive index n_1 , which is typically a prism glass, and the final medium (N) is the sensed layer having a refractive index n_N . Between these two media there could be a

number of layers such as chromium, gold, silver, silicon, graphene, etc., which are used to realise a plasmon resonance and to optimise the system in terms of sensitivity and affinity. The structure under consideration is depicted in Figure (3).

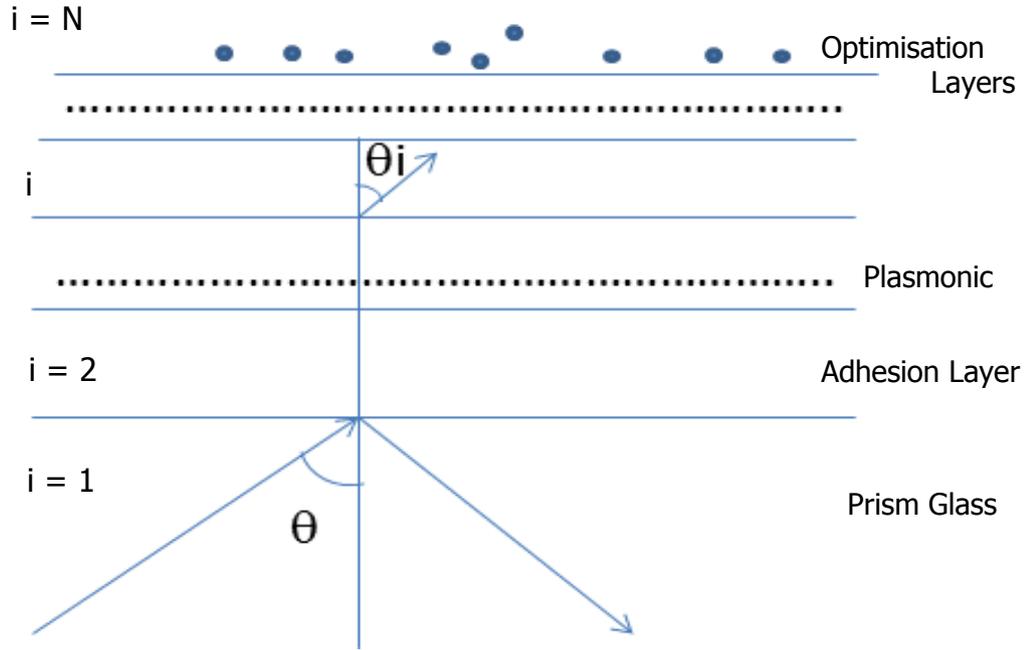


Figure 3 Schematic of the multi-layered (N-layer) system modelled for optimal SPR sensing.

The complex reflection r and transmission t parameters are found from equation:

$$\begin{pmatrix} 1 + r \\ (-1 + r) \cos \theta / n_1 \end{pmatrix} = \hat{M} \begin{pmatrix} t \\ -t \cos \theta_N / n_N \end{pmatrix} \quad (2)$$

Here θ is the angle of incidence, θ_N is the refraction angle in the last medium (sensed layer). The characteristic matrix M is composed of the corresponding matrices of the intermediate layers

$$\hat{M} = \prod_{i=2}^{N-1} \hat{M}_i \quad (3)$$

$$\hat{M}_i = \begin{pmatrix} \cos(\beta_i h_i) & \frac{j}{p_i} \sin(\beta_i h_i) \\ j p_i \sin(\beta_i h_i) & \cos(\beta_i h_i) \end{pmatrix} \quad (4)$$

$$\beta = k_0 n_i \cos \theta_i, \quad p_i = \frac{\cos \theta_i}{n_i}, \quad k_0 = \frac{2\pi}{\lambda} \quad (5)$$

Here λ is the wavelength, $j = \sqrt{-1}$, n_i , θ_i and h_i are refractive index, angle of refraction and thickness of the i -th layer, respectively. Monitoring the light reflected from the system, the change in refractive index of the sensed layer can be deduced in real time. An angle or wavelength modulation techniques for intensity and/or phase monitoring are used. In the case of angle modulation, which is considered here, the intensity and phase are plotted as functions of angle of incidence. The angle of minimum of $|r|$ corresponds to plasmon resonance and changes with the change in n_N . If the change in resonance angle is $\Delta\theta_{res}$ and the corresponding relative change in the refractive index is $\epsilon = \Delta n / n_N$ [24], the sensitivity of the method is defined as:

$$S = \frac{\Delta\theta_{res}}{\epsilon} \quad (6)$$

In practice, the sensitivity in (6) determined by local slope is multiplied by instrumentation parameter related to resolution. The equations (2)-(5) can be used to predict a rapid phase change near the resonance angle with change in ϵ . Typically, the phase change has a steeper slope over a limited range of ϵ . The sensitivity characteristics will be compared for basic systems considered below. From a theoretical point of view, a higher sensitivity can be achieved in thin silver films due to its narrower resonance [26], as compared to thin gold films. Thanks to its less reactive nature and ease of functionalisation, gold makes the most applicable metal in biosensing context.

For further modeling, the complex refractive index $n = \tilde{n} + jk$ of a number of materials (Cr, Ti, Ag and Au) are listed in Table 1 at the wavelengths available in the laboratory. For graphene, the refractive index is expressed by the following equation: $n = 3 + j(5.446\lambda)/3$ [33].

TABLE 1: Real and imaginary refractive index ($n = \tilde{n} + jk$) for Chromium, Titanium, Silver and Gold for three different wavelengths [32]

Wavelength λ (μm)	Cr		Ti		Ag		Au	
	\tilde{n}	k	\tilde{n}	k	\tilde{n}	k	\tilde{n}	k
0.405	1.43	3.54	1.55	2.15	0.173	1.95	1.65	1.956
0.664	3.48	4.36	2.29	3.05	0.14	4.15	0.166	3.15
0.850	4.31	4.32	3.08	3.31	0.152	5.721	0.198	5.63

3. PLASMONIC LAYERS

In most SPR systems the typical configuration is a glass prism with a 50 nm gold film which is responsive to the local gold-dielectric interface. Gold satisfies many of the plasmonic requirements for a sensor; it is easy to grow, is a good conductor (free electrons) and is chemically stable (it does not oxidise). Do any other materials satisfy these criteria? Leroy et al [27] used indium tin oxide (ITO) in a prism coupling experiment, where waveguide modes were used to explore how the refractive index of BaTiO₃ is responsive to the applied electric field. ITO is a common material today being both transparent and conductive – it is known as a transparent conducting oxide [28]. However, the most promising alternative plasmonic layer is silver. This is also a good electrical conductor, but is more reactive compared to gold, and easily oxidises (to form silver oxide). The first development of the system model is to compare the SPR response for gold and silver. For the same glass prism, the attenuated total reflections (ATR) were modelled for Au and Ag as shown in Figure 4 where the reflected intensity vs. angle of incidence is plotted. It is seen that both Au and Ag are suitable candidates for the plasmonic layer. It can be clearly seen that the reflectivity response with Ag as a plasmonic layer has a much narrow minima response.

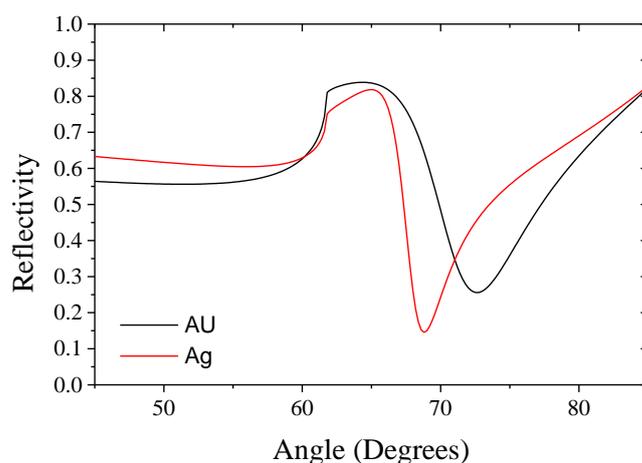


Figure 4. Reflection intensity response for a typical SPR system glass/Au/water (black) and glass/Ag/water (red) at a wavelength of 664 nm. Refractive index of water is 1.33. In each case the Ag or Au film thickness is 35 nm.

Au is the plasmonic layer of choice in most situations, the reason behind this is that Au is chemically stable, whereas Ag is quite reactive, forming AgO_2 , which degrades the SPR signal and is observed as a widening of the reflectivity response curve [29]. A number of theoretical works have looked at how to overcome this artefact and so develop a more sensitive system [30]. An obvious solution is to use a protective Au layer at silver interface with the sensed layer.

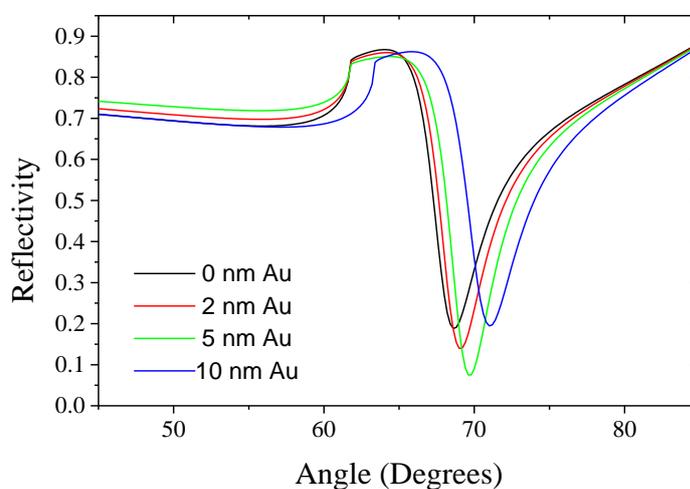


Figure 5. Reflected intensity in the plasmonic system 35 nm Ag / Au for different thicknesses of Au layer: 0, 2, 5, 10 nm. The wavelength is 0.664 nm.

Figure 5 shows the reflected intensity as a function of angle for 35nmAg/Au plasmonic system with the Au thickness as a parameter. For 5 nm Au layer, the resonance is deep and narrow which will result in high sensitivity and resolution. A further problem when using a metallic layer (such as Au) at the interface with the sensed layer is that molecules and particles do not have a high affinity for gold, which restricts their presence at the interface. Typically, an additional immobilisation layer is used. It was also proposed to make use of layers of graphene at the interface to improve affinity.

4. THE EFFECT OF THE ADHESION LAYER

To fabricate an SPR sensor using a gold plasmonic layer requires that a thin adhesion layer is grown onto the glass prism/substrate [31]. This adhesion layer is around 2-3 nm thick and is normally chromium or titanium. These two metallic films have quite different optical and electronic properties as seen from Table 1. In Figure 6 it is shown that the adhesion layer has a significant effect on the response in the phase domain; the use of a titanium adhesion layer yields a sharper phase change at resonance. Using graphene layers makes the resonance minima deeper, improving the sensitivity and resolution.

By using phase sensitive detection with a lock-in amplifier the SPR system will be better equipped to see the SPR response for extremely low refractive index changes at the metal-dielectric interface.

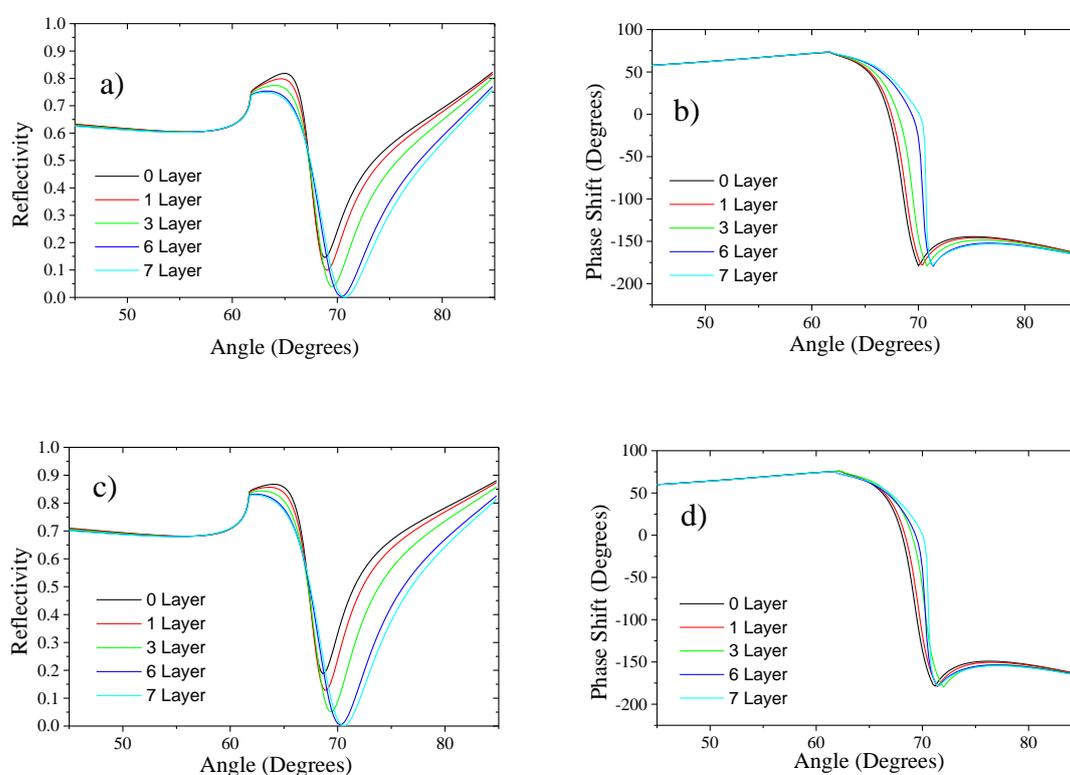


Figure 6. Effect of an adhesion layer on SPR parameters in 2 nm Cr(Ti) / 35 nm Ag / Graphene for various numbers of graphene layers (1 Layer = 0.34 nm). Cr in (a) and (b), Ti in (c) and (d). Reflected intensity in (a) and (c) and phase shift in (b) and (d). The wavelength is 0.664 nm.

5. GRAPHENE LAYERS FOR INCREASED DETECTION SENSITIVITY

Graphene has been hailed as the wonder material of the 21st century that will impact the way nano and micro-electronic devices perform through to improving the performance of photo voltaic cells used for solar energy applications [33, 34]. It does indeed have some amazing properties, and if a layer is wrapped it can become a carbon nano tube (CNT), or it can be in the form of sphere

(fullerenes or 'bucky balls'). CNTs are also of interest as they can be found in anti-ageing creams and have been shown to be damaging to the major organs of rainbow trout [35]. However, in this paper the focus is on graphene layers for SPR sensing. The model developed previously is extended to include graphene on both silver and gold thin films. Figures 6-8 show the results from this change.

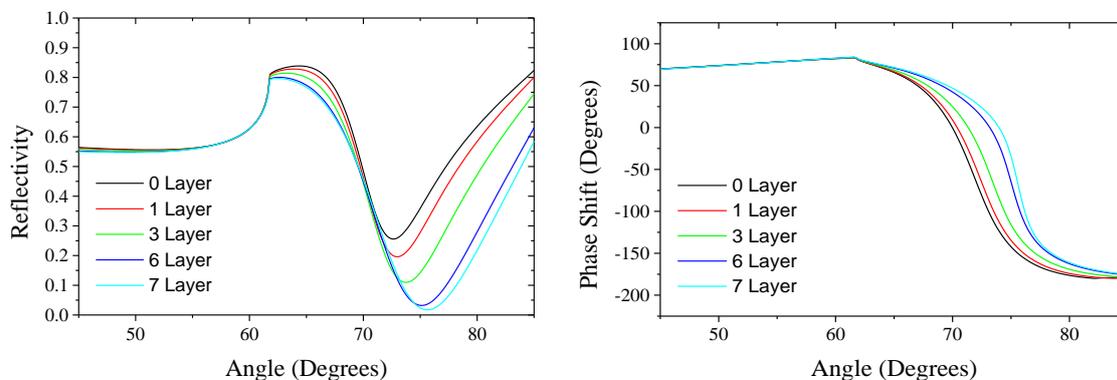


Figure 7. Intensity (left) and phase (right) for 2 nm Cr / 35 nm Au / graphene.

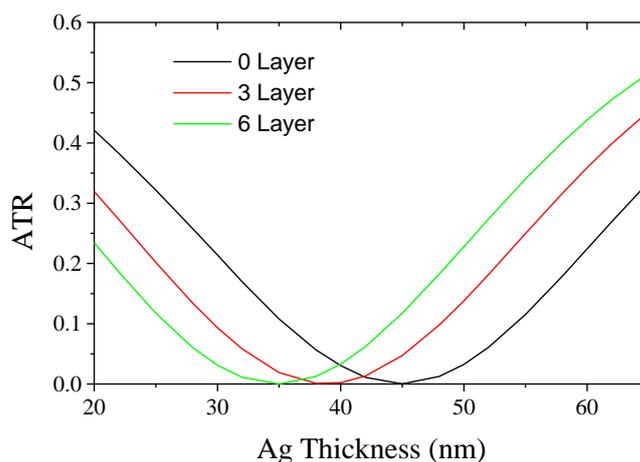


Figure 8. SPR response as a function of Ag film thickness for different number of graphene layers at a wavelength of $0.664 \mu\text{m}$.

The results here are highly encouraging, Figures 6-7 show that for both Ag and Au films the sensitivity is improved as the minimum reflectivity at the SPR angle obtained for metallic layer of 35 nm thick decreases with increasing the number of graphene layers. This process is accompanied by widening the resonance curve which would affect the resolution, so optimal number of graphene layers is needed. SPR arises from the exponentially decaying evanescent wave which suggests sensitivity improves when the metal-dielectric interface is closer to the prism. Furthermore, it means that now the SPR sensor chip can be fabricated using a 35 nm silver thin film to take advantage of its higher sensitivity, with the graphene layers improving sensitivity by virtue of improved affinity whilst also being a protective layer to minimise, or even stop oxidation of the silver film. If oxidation or reactivity persists then an alternative sensor chip is proposed. This configuration would comprise of the Ag plasmonic layer, with a 3-5 nm Au film as a protective layer. The optimum layer thickness will be determined and then explored with graphene. The sensor chip will be glass / Ag or Au / graphene. Figure 8 shows the SPR response in Ag/graphene system as a function of Ag thickness for different number of graphene layers. It is seen that for a given Ag thickness a deeper resonance requires an optimal number of graphene layers.

6. LOCALISED SURFACE PLASMON RESONANCE (LSPR)

In SPR, resonance can occur at a particular electromagnetic frequency ω when $\epsilon_r = -2 \epsilon_m$ [36]. Gold and silver nanoparticles are of interest here and the SPR condition can be obtained in the visible spectrum. When bulk materials (thin films) are compared to nanoparticles the situation is different. These noble metal particles, being less than 100 nm in size, are smaller than the wavelength of light used, and enable large optical field enhancements through the optical confinement phenomenon. This is because the free electrons of noble metal nanoparticles interact with visible light giving rise to the phenomenon of localized surface plasmon resonance (LSPR). These enhanced local electromagnetic fields near the surface of the nanoparticle are responsible for the intense signals observed in surface enhanced spectroscopy [37].

This localised phenomenon can be used to sense individual particles without using plasmonic layers. However, if the particle size is much smaller than the wavelength, LSPR condition will not be satisfied. Yet, using the previous plasmonic system low concentrations of silver nanoparticles can be sensed since these particles change the refractive index of the sensed layer. Since we are interested in diluted systems, the permittivity of particles in aqueous solution can be evaluated within the effective medium theory [35].

$$\epsilon_N = \epsilon_d + 4\pi v \alpha \quad (6)$$

where ϵ_d is the permittivity of the aqueous solution, v is the particle volume concentration and α is the dielectric polarizability of a particle which depends on its size, shape and material. For a spherical particle of size much smaller than the wavelength:

$$\alpha = \frac{3}{4\pi} \frac{\epsilon_d (\tilde{\epsilon}_m - \epsilon_d)}{2\epsilon_d + \tilde{\epsilon}_m}, \quad (7)$$

$$\tilde{\epsilon}_m = \epsilon_m f(k_m a), \quad f(x) = \frac{1}{x^2} - \frac{1}{x \tan x} \quad (8)$$

where ϵ_m , $k_m = k_0 / \sqrt{\epsilon_m}$ and a are metallic permittivity, wave number and radius of metal particles.

Figure 9 shows the reflected intensity and phase as functions of Ag particle concentration for plasmonic system 35 nm Ag/6 layers of graphene. If the angle corresponding to the ATR minimum is plotted as a function of Np % concentration the response is linear with a responsivity of 393.75 degrees per concentration %. This is shown in Figure 10.

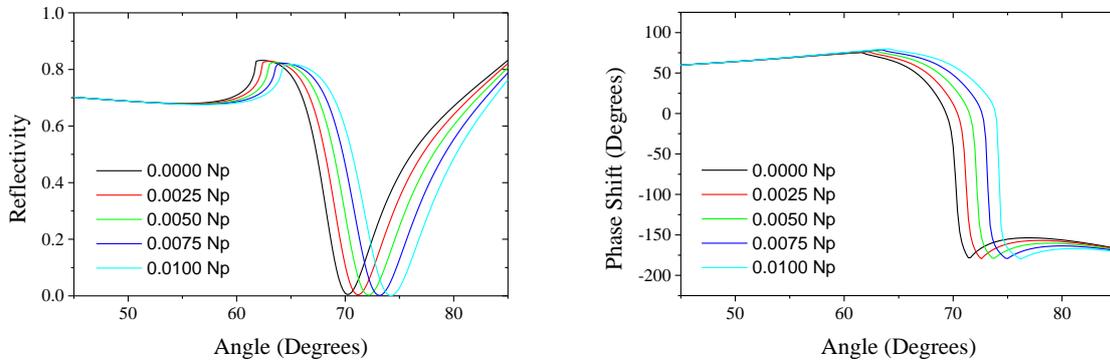


Figure 9. SPR response (ATR and phase) as function of Ag particle concentration for a 35 nm Ag silver plasmonic layer and 6 layers of graphene, at a wavelength of $0.664 \mu\text{m}$. The particle size is 40 nm.

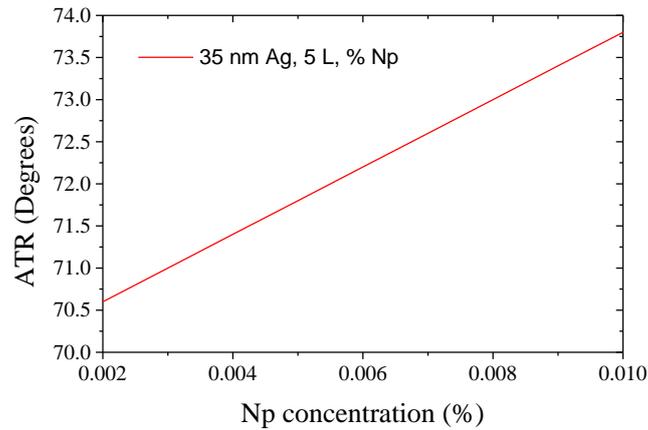


Figure 10. Resonance angle (minimum of reflectivity) as a function of nanoparticle (Np) concentration (%).

7. PHASE SENSITIVITY

The plasmonic system for detecting the presence of silver nanoparticles has been comprehensively modelled, based upon sensor chip structures that can be fabricated in the laboratory. In the majority of SPR systems the detection is based upon detection of the angular shift in the resonance angle by measurement of the attenuated reflected signal. The SPR is a second order system undergoing a 180° phase shift as the response passes through the resonant condition. We consider a sensor structure comprising 2 nm Ti + 35 nm Ag+ n layers of graphene followed by water ($\bar{n} = 1.333$), which can contain Ag nanoparticles. The results of this simulation are shown in Figure 11. For 6 layers of graphene, two cases are considered, one with water alone, and the other with silver nanoparticles introduced at the metal/dielectric interface.

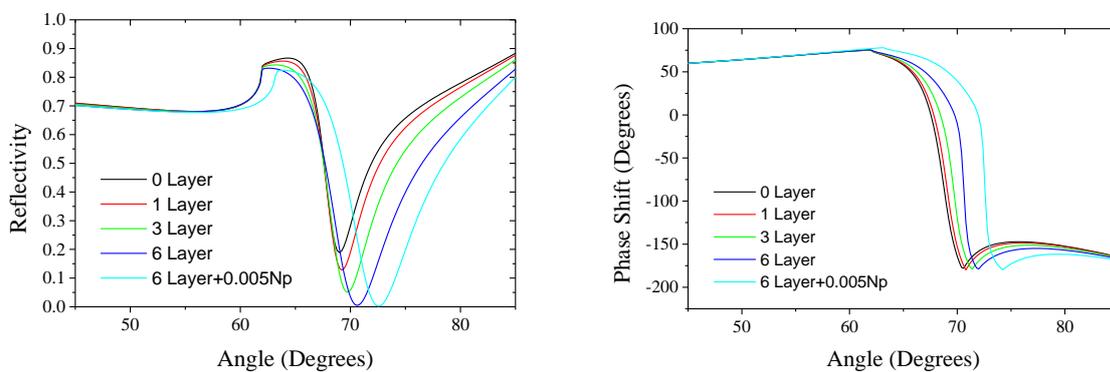


Figure 11. SPR reflectivity and phase response in Ti/Ag/graphene system for different number of graphene layers. The influence of nanoparticle presence is shown for 6 graphene layers.

To explore the phase sensitivity, a phase modulation with respect to small changes in refractive index at an angle close to the resonance angle can be utilised. Water has a refractive index $\bar{n} = 1.333$ and

so the model explored the phase response to changes in the permittivity when the refractive index changes from $\tilde{n} = 1.333$ to $\tilde{n} = 1.336$. Figure 12 shows the response for the phase shift with increasing refractive index, for different number of graphene layers. There is approximately a 4 degree phase change associated with each layer of graphene. The sensitivity for the phase response is 2.3×10^3 degrees per refractive index unit change (real part), which is almost 5 times higher than the amplitude sensitivity.

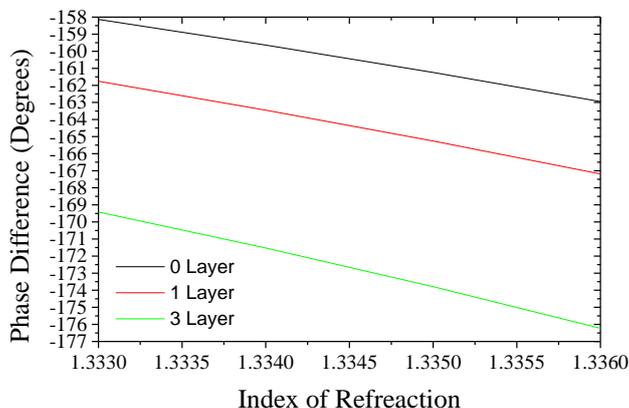


Figure 12. SPR phase response for changing permittivity at the metal-dielectric interface, for 0, 1 and 3 layers of graphene.

8. DISCUSSION

This research has been focused on the development of a model that is both adaptable and robust, and able to simulate the SPR response to detect metallic (conducting) nanoparticles. In this case the particles of interest are silver nanoparticles, which are increasingly used in consumer products, yet highly toxic to aquatic life. The model developed was initially based upon the typical configuration of a gold plasmonic layer grown on a glass prism. In order to optimise the simulated system for this application a number of areas have been addressed. A model where the SPR reflectivity response using gold or silver as the plasmonic layer showed that silver produces a sharper resonance response. To grow silver or gold onto glass requires a 2-3 nm adhesion layer. The simulation was used to explore the influence of the adhesion layer; in this case 2 nm of either Cr or Ti was used. The simulation showed that for a silver plasmonic layer the reflectivity response was quite similar.

However, the phase response for the Ti adhesion layer was much sharper than with Cr. Furthermore, silver is reactive and oxidises easily, which is detrimental to the SPR response. To overcome this, a protective layer is required. This could simply be a 2-3 nm layer of gold, or more usefully a number of layers of graphene. Simulations showed that adding a protective gold film is also detrimental to the SPR response. With graphene the simulations were extremely encouraging. Graphene revealed two interesting features. Firstly, graphene does not affect the sharpness of the SPR response. Secondly, by determining the thickness of the plasmonic layer that produces the minimum reflectivity without graphene, which was 45 nm, with graphene it was reduced to 35 nm. Thus, the sensor layer containing nanoparticles will be much closer to the metal-dielectric interface. This is expected to increase the SPR sensitivity. The numbers of layers of graphene were also varied and it was shown that changing from zero layers to seven layers was also influential on the SPR response. The phase response was shown to be sensitive to the number of graphene layers and to be a linear function of the SPR minimum, as the refractive index was varied from 1.333 to 1.336; a 0.1 % change.

Finally, we also explored the detection of silver nanoparticles. Metallic nanoparticles, although much smaller than the wavelength, are able to support localised plasmonic resonance. This functional

property usually enhances SPR sensitivity, but here it was used to detect the particles themselves. The effective permittivity of water and small percentage of Ag particles were modelled and used to explore the response, in reflectivity and phase, to increasing concentrations of Ag particles. The outcomes of this simulations revealed that there is a linear response to reflectivity with particle concentration.

9. CONCLUSIONS

A brief overview of SPR and LSPR in nanoparticles for biomaterial sensing has been detailed. Theoretical model for multiple layers of metals has been developed for SPR. This analysis shows that Ag offers better sensitivity than Au, but the latter is not reactive and therefore the material of choice in plasmonic sensing. We have also presented simulation results which demonstrate that functionalised graphene offers higher sensitivity and biomaterial affinity, due to its inherent electronic and optical as well as mono-atomic thickness. In addition, a new approach to improving sensitivity has also been proposed using a lock-in amplifier technique to measure intensity as well as the phase of the reflected optical signal. This combined with the theoretical models detailed here, may potentially offer a route to single molecule detection.

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