# Directional Surface Plasmon Coupled Luminescence for Analytical Sensing Applications: Which Metal, What Wavelength, What Observation Angle?

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The ability of luminescent species in the near-field to both induce and couple to surface plasmons has been known for many years, with highly directional emission from films (Surface Plasmon Coupled Luminescence, SPCL) facilitating the development of sensitive near-field assay sensing platforms, to name but just one application. Because of the near-field nature of the effect, only luminescent species (fluorescence, chemiluminescence and phosphorescence) within a few hundred nanometers from the surface play a role in coupling, which in terms of biosensing, provides for limited penetration into optically dense media, such as in whole blood. Another attractive feature is the highly polarized and angular dependent emission which allows both fixed angle and wavelength dependent emission angles to be realized at high polarization ratios. In this paper, a generic procedure based on theoretical Fresnel calculations, which outlines the step-by-step selection of an appropriate metal for SPCL applications is presented. It is also shown that 11 different metals have differing properties in different spectral regions and offer either fixed angle or wavelength-dependent angular shifts in emission. In addition, it is shown that both chemiluminescence and phosphorescence can also be observed in a highly directional manner similar to coupled fluorescence.

Surface plasmon spectroscopy, a technique based on the surface plasmon resonance (SPR) phenomenon, has been proven to be a very useful analytical tool for the monitoring of biological processes at the metal/dielectric interface.<sup>1-4</sup> The SPR phenomenon utilizes the interactions of light with thin metal films and affords for label-free detection of biorecognition events.<sup>5</sup> When an analyte or biological material of interest is brought within  $\approx$ 200 nm of the metal surface via specific chemical or biological events, a change in the evanescent field of the surface plasmon mode near the metal surface (typically in the form of reflectance of light)

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from the surface), which is directly related to the extent of biorecognition events, can be observed.<sup>6,7</sup> It is important to note that the SPR phenomenon can also be used for characterization of interfaces and thin films,<sup>8</sup> monitoring of kinetic processes,<sup>9</sup> and so on. Despite its usefulness, surface plasmon spectroscopy suffers from a lack of sensitivity in the detection of very small analytes and proteins because of the very dilute surface coverage on the metal surface. To alleviate this problem, a new technique called surface plasmon fluorescence spectroscopy (SPFS),<sup>10,11</sup> which incorporates luminescent species in connection with surface plasmon spectroscopy, was introduced in 2000.<sup>10,11</sup>

In SPFS, the extent of an analyte of interest or other biological materials is monitored by the change in luminescent emission as a result of specific biorecognition events occurring on the metal surface.<sup>10,11</sup> Although one can still collect the reflectance data at the same time, luminescence data are always more sensitive. In a typical SPFS-based application, one or more of the binding partners in a bioassay are attached to the metal surface, and the luminescent species that is covalently linked to the other binding partner is brought in close proximity to metal surface.<sup>12</sup> Subsequently, the luminescent species are excited using an appropriate choice of excitation source including lasers,13 halogen lamps,14 or LEDs.<sup>15</sup> In SPFS, the excitation of luminescent species can be achieved using two different experimental configurations:<sup>13</sup> (1) Reverse Kretschmann (RK) configuration or (2) Kretschmann (KR) configuration. In the RK configuration, luminescent species are directly excited by the incident excitation source and the resulting luminescence emission couples to surface plasmons. In the KR configuration, the excitation light enters through the prism

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and generates the surface plasmons in the metal film which in turn excite the luminescent species within a certain distance (typically  $\approx 200$  nm) from the surface. The luminescence emission can be collected either from the sample side (also referred to as free-space emission) or from the back of the metal thin film at a specific observation angle (referred to as surface plasmon coupled luminescence (SPCL)): for fluorescence, chemiluminescence, and phosphorescence this is surface plasmon coupled fluorescence (SPCF), surface plasmon coupled chemiluminescence (SPCC), and surface plasmon coupled phosphorescence (SPCP), respectively. When a hemispherical prism is employed, the SPCL emission appears as a "ring" because of the symmetry conditions of the near-field surface excited dipoles. The SPCL observation angles coincide with the metal's angle of minimum reflectivity and vary with the type of metal used, subsequent overlayers present on the metal films, and wavelength of the excitation source.

In publications on SPCL to date, the use of zinc<sup>13</sup> and aluminum<sup>14</sup> thin films in the UV spectral range, and nickel,<sup>16</sup> zinc<sup>13</sup> and silver<sup>12,17</sup> thin films in the visible spectral range were demonstrated. Nickel,<sup>16</sup> gold,<sup>12</sup> and copper<sup>18</sup> thin films were also shown to work in the red spectral region. Originally used for surface plasmon spectroscopy, theoretical Fresnel calculations are a great tool for the prediction of the interactions of light with metal thin film also for SPCL. The optimum thickness of a metal film at any wavelengths of light can be determined using Fresnel calculations. One can also determine the range of wavelength of light that the metal thin film can be used for. Despite the existence of numerous publications on SPCL-based use of different metals. most of the information is scattered, and there is not a single publication that offers an overall procedure for the selection of an appropriate metal thin film for the desired SPCL-based applications.

In this paper, we subsequently present a procedure based on theoretical Fresnel calculations that provides researchers with the necessary information for the selection of appropriate metal thin films for SPCL. Since SPCL utilizes the SPR phenomenon, we first briefly discuss the SPR phenomenon separately and also in conjunction with luminescent species (near-field dipoles). Subsequently, we discuss the overall procedure for the selection of metals for a typical SPCL study using two metals as examples. In addition, we summarize the results for a total of 11 surface plasmon supporting metals, a few of which have been experimentally demonstrated in the literature. Fresnel reflectivity curves used for the determination of optimum thickness and the spectral range for all 11 metals are provided. The framework for a typical SPCL study we present here will likely be useful to those researchers already working or to those thinking about entering into this area of research.

#### **THEORETICAL CONSIDERATIONS**

Since SPCL is related to the SPR phenomenon, it is pertinent to briefly discuss the theory describing the interactions of light with metal surfaces. One can find a detailed discussion of the SPR phenomenon in an excellent review paper by Knoll.<sup>19</sup> The discussion on SPR in this work is aimed to be introductory rather than being repetitive and exhaustive. Figure 1A shows the propagation of light across and metal-sample interface, which is employed in surface plasmon spectroscopy. Gold is typically the metal of choice in this technique, and the dielectric constant of gold is greater than the dielectric constant of air. It is important to note that surface plasmons can only be generated by light that has an electromagnetic component normal to the surface (zdirection), or *p*-polarized light (Transverse Magnetic). Since s-polarized light (also referred to as Transverse Electric waves) propagating along the x-direction possess only an electric field parallel to the surface (y-direction) it is canceled out by its mirror image on the surface, therefore surface plasmons cannot be induced by s-polarized light. The p-polarized light source generates an evanescent electromagnetic wave across the metal-sample interface, along the x-axis (Figure 1B), and the electric field component can be described by

$$\vec{E}_{1} = \vec{E}_{10} e^{i(\vec{k}_{x1}\vec{x} + \vec{k}_{z1}\vec{z} - \omega t)}$$
(1)

in metal (medium 1), z < 0, and

$$\vec{E}_2 = \vec{E}_{20} \mathrm{e}^{\mathrm{i}(\vec{k}_{x2}\vec{x} + \vec{k}_{z2}\vec{z} - \omega t)} \tag{2}$$

in sample (medium 2), z > 0, where  $\vec{E}_1$ ,  $\vec{E}_2$ ,  $\vec{k}_{x1}$ , and  $\vec{k}_{x2}$  are the wavevectors in the *x*-direction and  $\vec{k}_{z1}$  and  $\vec{k}_{z2}$  are the wavevectors in the *z*-direction, and  $\omega$  is the angular frequency.

At the metal-sample interface  $\vec{E}_1 = \vec{E}_2$  (a condition for SPR), which is followed by

$$k_{\rm x1} = k_{\rm x2} = k_{\rm x}$$
 (3)

Since medium 1 is metal, which has a complex dielectric function ( $\varepsilon_{\rm m} = \varepsilon_{\rm m}' + i\varepsilon_{\rm m}''$ ) and medium 2 is sample ( $\varepsilon_{\rm s} = \varepsilon_{\rm s}' + i\varepsilon_{\rm s}''$ ), eq 3 can be expressed also as

$$k_{\rm x1} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_{\rm m} \times \varepsilon_{\rm s}}{\varepsilon_{\rm m} + \varepsilon_{\rm s}}} \tag{4}$$

The other condition for SPR involves the incident light  $(k_{\rm P})$ , which is used to generate surface plasmons when its *x*-axis component  $(k_{\rm P,x})$  equals the propagation vector for the surface plasmon  $(k_{\rm x1})$ .

$$k_{\mathrm{P,x}} = k_{\mathrm{x1}} \tag{5}$$

where,  $k_{\rm P} = k_0 n_{\rm P}$  and  $k_{\rm P,x} = k_0 n_{\rm P} \sin \Theta_{\rm SP}$ .  $k_0$  is the propagation constant of an electromagnetic wave in a vacuum, n is the refractive index of the medium,  $\Theta_{\rm SP}$  is the angle of incidence in the metal for SPR to occur. Then,

$$k_{\rm x1} = k_0 n_{\rm P} \sin \Theta_{\rm SP} \tag{6}$$

It is important to discuss the implications of eqs 1–6. When the incident light is impinging on the metal from air or vacuum

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Figure 1. (A) Schematic representation of an experimental setup for Surface Plasmon Resonance (SPR) measurements carried out with a hemispherical prism. (B) Schematic depicting the interactions of incident light with a metal film. (C) SPR reflectivity curves for a 50 nm gold film illuminated with a 594 monochromatic light source. Fresnel calculations were employed to generate these curves. The reflectivity curves for the gold film coated with 11-mercaptoundecanoic acid (MU), followed by a carboxylated-dextran layer and finally with an antibody.

 $(n_{\rm P} = 1)$ , the maximum value for  $k_{\rm P} = k_{\rm x,1} = k_0$ . A close look at the complex dielectric functions (readily found in the literature) in eq 4 reveals that  $\varepsilon_{\rm m}' < 0$ , thus for SPR,  $k_{\rm x,1} > k_0$ . That is, surface plasmons cannot be induced with light incident from air or medium (in Reverse Kretschmann, RK, configuration) with dielectric constants smaller than the metal. Surface plasmons in the metal can only be induced when  $k_{\rm P}$  is increased by passing the incident light through a prism (refractive index >1.5) at an angle of  $\Theta_{SP}$ , as shown in Figure 1A). Because of the complex nature of  $\varepsilon_m$  and  $k_x$ , surface plasmon modes propagate along the metal/sample interface at a finite length, dependent on the imaginary component of  $k_x$ . In addition, the evanescent wave has a maximum amplitude at the interface (z = 0) and decays exponentially into the sample and the metal. The penetration depth of this light into the dielectric medium is calculated to be a few hundred nanometers.<sup>10</sup>

The solutions to eqs 1–6 can be found by performing *theoretical Fresnel calculations* by considering the different optical properties of each dielectric layer and their respective thicknesses, surface plasmon resonance conditions. A typical result of these calculations is the so-called reflectivity curves. The reflectivity curves is a result of surface plasmon excitation by light, and has a narrow "dip" at a certain angle with a minimum value reaching close to zero in the most ideal situation. The half-width of the reflectivity curve for metals is different, mostly because of their differences in the value of the imaginary part of their dielectric

function. Figure 1C shows typical reflectivity curves for a gold film and subsequent dielectric layers deposited on top of the gold film. The reflectivity minimum for gold occurs at 45.5° and is shifted toward wider angles with the addition of subsequent overlayers. The extent of shift in the angle of minimum reflectivity predominantly depends on the thickness of the additional dielectric layers. While relatively small molecules like mercaptoundecanoic acid and dextran results in  $0.2^{\circ}$ , a biomolecule like an antibody causes a shift of  $\approx 3^{\circ}$  in the reflectivity minimum.

It is also known that the electric field is significantly enhanced at the angle of minimum reflectivity (SPR angle).<sup>10</sup> The electric field is enhanced up to 50 times for silver and 16 times for gold. This is in part relevant to the SPFS technique, where luminescent species are placed in close proximity to the metal surface and excited at the SPR angle. Luminescent species can be excited either from the sample side (RK configuration) or through a prism (Kretschmann, KR, configuration), cf. Figure 2. Unlike far-field excitation light impinging on the metal surface from the sample side, luminescent species (dipoles) within  $\approx 200$  nm (Figure 3A) can induce/couple to surface plasmon in metals, regardless of the mode of excitation space. Subsequently, both the free-space and the SPCL emission can be collected. While the free space emission is isotropic the SPCL is highly directional and preferentially p-polarized (Figure 3A,B). The SPCL emission can be observed at the angles coinciding with the angle of reflectivity minimum and appears as a "ring" from the back of the metal film



**Figure 2.** Schematic representation of an experimental setup for Surface Plasmon Coupled Luminescence (SPCL) measurements carried out with (A) a hemispherical prism used to collect the "ring" of emission and from metal substrates (B) a 45-degree prism that affords for Kretschmann (KR) and Reverse Kretschmann (RK) geometries to be used. SPCL is a general term that includes surface plasmon-coupled fluorescence, chemiluminescence, and phosphorescence, i.e, it includes SPCF, SPCC, and SPCP, respectively.

(Figure 3A,B). Figure 3C shows a typical reflectivity curve for a gold film and SPCL emission from a fluorophore collected from the back of the gold film.

As reported before,<sup>10</sup> the maximum luminescence intensity is found at a slightly lower angle than the angle of minimum reflectivity. This is attributed to the difference in the phase of electromagnetic waves reflected directly from the metal surface (excitation light) and the re-radiated light (luminescence emission) from the metal surface. For metals with a large imaginary part of their dielectric function, the phase difference is larger. Consequently, the difference between the angle of the reflectivity minimum and the angle where the maximum luminescence intensity is observed becomes larger.<sup>10</sup>

It is also important to note the distance-dependent nature of the interactions of luminescent species with surface plasmons in metal thin films. For a very short separation distance (d < 10 nm) between the luminescent species and the metal surface, the luminescence emission is mostly transferred to surface plasmons in a non-radiative fashion and is subsequently dissipated as heat by the metal (quenching).<sup>20</sup> For intermediate separation distances (10 to 200 nm), the excited luminescent species can couple to surface plasmons and be emitted as a "ring or cone" from the back of the metal film (SPCL). For larger separation distances (in the far-field >200 nm), the luminescent species do not interact with the surface plasmons and only free-space emission is observed in the RK configuration or no emission is observed in the KR configuration. It is also important to note that the penetration depth of light varies with the type of metal; thus one can observe SPCL and free-space emission from luminescent species placed at distances larger than 200 nm.<sup>16</sup>

Another important aspect of the luminescence intensity measurements in SPCL is the angle of observation. The luminescence measurements for the monitoring of kinetic binding events are typically recorded at a fixed observation angle. When the



**Figure 3.** (A) Schematic depiction of the SPCL phenomenon. SPCL emission can be observed at the angles coinciding with the angle of reflectivity minimum and appears as a "ring" from the back of the metal film. (B) Angular distribution of emission from a fluorophore on a metal thin film. Free-space emission from the sample side is collected from the top and SPCL is collected through the prism (bottom) (C) Reflectivity curve of *p*-polarized light at 594 nm for 50 nm thick gold substrates overlaid with normalized *p*-polarized fluorescence intensity from a fluorophore.



Figure 4. Flowchart depicting the steps for a SPCL study. SPCF-surface plasmon coupled fluorescence; SPCC-surface plasmon coupled chemiluminescence; SPCP-surface plasmon coupled phosphorescence.

luminescent species are brought to the metal surface as part of specific binding events between biomolecules with molecular sizes sufficient to induce a significant shift in the SPR angle, the measured intensity becomes non-linear. That is, as the SPR angle is shifted the corresponding luminescence intensity levels off. Subsequently, the correction of the kinetic luminescence measurements, especially when the thickness of the adsorbed layer is larger than 2 nm, is required.<sup>10</sup> On the other hand, such complications can be averted by employing metals which do not show a shift in the SPR angle with increasing thickness of the adsorbed layer. The research in our research laboratory has shown that luminescence measurements from metals such as iron and nickel can be carried out at a fixed observation angle without the required correction of luminescence data.<sup>11</sup> These results will be discussed in the next section of the text.

#### **RESULTS AND DISCUSSION**

In this section, a procedure based on theoretical Fresnel calculations that outlines the necessary steps for the selection of an appropriate metal thin film for SPCL applications will be discussed in detail. Figure 4 shows a flowchart depicting the multiple steps involved in determining the optimum thickness of the metal and the wavelength range that the selected metal can operate using theoretical Fresnel calculations. From these calculations, the observation angle and the effect of additional overlayers can be determined. One can prepare or procure the selected metal thin with the predetermined specifications and utilize them in the desired applications based on the SPCL phenomenon.

Table 1 presents a list of metals which were either used or can be potentially used in SPCL applications. Table 1 also lists the corresponding optimum metal thickness, the operational wavelength range and the observation angle for SPCL. These parameters were determined using theoretical Fresnel calculations in this study or collected from literature. Figures F5–F9 (and Supporting Information, Figures S1–S9) show the results of Fresnel calculations for all the metals listed in Table 1. As shown in Table 1 various thicknesses of metals are used in SPCL applications. For example, the optimum thickness for gold, silver and copper thin films is >40 nm and other metals have an optimum thickness of 15-20 nm. While the reasons for this observation are currently not completely understood, it is thought that the thickness of the metal film depends on the dielectric function of the metal. For gold, silver, and copper, the imaginary part of the dielectric function ( $\varepsilon_m''$ ) is smaller than for the other metals. The imaginary part of the dielectric function is associated with the damping of the excited mode, and hence for larger  $\varepsilon_m$ " the dissipation of the surface plasmon polariton wave is larger, and vice versa. The surface plasmon polariton wave is a non-radiative evanescent wave extending into the dielectric layer, and this excited mode decays exponentially to the metal (and to the dielectric layer) in a damped oscillatory fashion. Subsequently, the extent of damping of the excited mode is affected by the value of  $\varepsilon_m$ ". In this regard, to obtain optical field intensity comparable to gold, silver, and copper, the thickness of the metals with large  $\varepsilon_m$ " should be less than gold, silver, and copper. It is important to note that the wavelengthdependent dielectric functions for most metals are available in the CRC Handbook of Chemistry and Physics.<sup>21</sup> In addition, these functions can be determined experimentally for other metals.22

A detailed look at Table 1 reveals that these metals can be employed in SPCL applications that cover a wide spectral range from 276 to 1500 nm. The selection of the wavelength range was based on the value of the minimum reflectivity of *p*-polarized light at the SPR angle, <0.2, above which the background intensities are expected to reach larger values at all angles. It is also

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#### Table 1. List of Metals Used in Surface Plasmon Coupled Luminescence (SPCL) Applications<sup>a</sup>

No.	Metal	Application	Metal Thickness, nm	SPCL Wavelength Range, nm	SPCL Observation Angle	Reference
1	Chromium	Fluorescence	20	276-517	Variable: 50-80	NP
2	Aluminum	Fluorescence	20	280-600	Variable: 42-46	NP
3	Palladium	Fluorescence	15/20	300-800	Variable: 45-70	NP
4	Zinc	Fluorescence Chemiluminescence	30	305-545	Variable: 45-68 Variable: 30-60	12
5	Nickel	Fluorescence Chemiluminescence	15/20	344-1240	Variable: 50-70 Variable: 50-70	15
6	Rhodium	Fluorescence	15	344-1240	Variable:45-75	NP
7	Silver	Fluorescence Chemiluminescence	40	413-620	Variable: 45-60	17
8	Gold	Fluorescence Phosphorescence	50	496-886 650	Variable: 45-60 65	10,13
9	Iron	Fluorescence Chemiluminescence	15	496-886	Fixed: 65 Fixed: 65	NP
10	Copper	Fluorescence	40	521-659	Variable: 55-70	18
11	Platinum	Fluorescence	15	800-1500	Variable: 50-70	NP

<sup>a</sup> NP-not published.



Figure 5. (Step 2) Determination of the thickness of metal substrates for SPCL. Fresnel reflectivity curves of *p*- (top) and *s*- (bottom) polarized light at (A) 620 for iron thin films and (B) 633 nm for gold thin films.

interesting to note the metals can be divided into three categories with respect to the spectral range that can be employed. Metals listed as 1-6 in Table 1 can be used in the UV, visible, and IR spectral regions. Metal listed as 7-10 can be used in the visible and red spectral regions. Platinum (listed as no. 11) can be used in the near-IR and IR spectral regions. Within all 11 metals, only

nickel and rhodium can find use in the widest spectral range (344-1240 nm). Chromium and zinc thin films have a narrow operational spectral range ( $\approx 200 \text{ nm}$ ).

Another interesting point is the observation angle, where the directional SPCL intensity can be measured. As described in the previous section, the SPCL angle coincides with the angle of



**Figure 6.** (Step 3–4a: Fixed SPCL Angle) Determination of the wavelength range for SPCL. Wavelength-dependence of reflectivity curve for 15 nm iron thin films. Fresnel calculations were employed to generate these curves.



Figure 7. (Step 3–4b: Variable SPCL Angle) Determination of the wavelength range for SPCL. Wavelength-dependence of reflectivity curve for 50 nm gold films. Fresnel calculations were employed to generate these curves.



Figure 8. (Step 5: Add Overlayer) Determination of the wavelength range for SPCL. Reflectivity curves for (A) a 15 nm iron film and (B) a 50 nm gold film with various thicknesses of poly vinyl alcohol (PVA) overlayer. Fresnel calculations were employed to generate these curves.

minimum reflectivity (with a slight shift to lower angles). As listed in Table 1, theoretical Fresnel calculations predict that the SPCL observation angle should occur at a variable range of angles, except for iron thin films. The SPCL angle is narrow typically for metals with low  $\varepsilon_{\rm m}'/\varepsilon_{\rm m}''$  ratio ( $\varepsilon_{\rm m}''$ , imaginary component of the dielectric function;  $\varepsilon_{\rm m}'$ , real component of the dielectric function). For metals with high  $\varepsilon_{\rm m}'/\varepsilon_{\rm m}''$  the angle becomes broader more than 25° and shifts, such as for chromium and palladium. On the other hand, the SPCL observation angle for iron thin films does not shift with wavelength and occurs at a fixed angle of 60°. The concept of fixed observation angle over a wide spectral range is attractive in the potential incorporation of metal thin films into existing luminescence spectroscopy techniques.

The implementation of the procedure described for the appropriate selection of optimum parameters for metal thin films in Figure 4 is demonstrated with two examples in Figures F5–F9. In this regard, gold and iron thin films, which show variable and fixed SPCL observation angles, are chosen. As indicated in Step 2 of the procedure, the optimum thickness of metal film can be determined by carrying out Fresnel calculations at a fixed wavelength and comparing the reflectivity curves for several thicknesses. It is known that metals form a continuous thin film on planar substrates when the thickness of the films is >15 nm,<sup>23</sup> below which the metals are mostly deposited as particulate films. With this information in mind, the calculated reflectivity curves for iron and gold thin films  $\geq 15$  nm using 620 and 633 nm light

are shown in Figure 5. The criterion for the selection of the optimum metal thin film thickness is based on the smallest value of the reflectivity minimum for *p*-polarized at the SPR angle. Since s-polarized light cannot induce surface plasmons, the reflectivity curves for s-polarized is considered only in the evaluation of the extent of background light (transmitted light not coupled to surface plasmons). As shown in Figure 5, the smallest value of the reflectivity minimum occurs for 15 and 50 nm for iron and gold thin films, respectively. One can repeat this procedure for multiple wavelengths to confirm the selection of optimum thickness of the metal thin film. In the process of selection of the optimum thickness the extent of s-polarized light has to be considered, which is 0.4 and 0.95 for iron and gold thin films at the SPR angle, respectively. That is, SPCL measurements from iron thin films are expected to contain more background light than the identical measurements from gold thin films. It is also important to note the background light can to some degree be eliminated by placing a polarizer in front of the detection optics.

Step 3 in the procedure is the determination of wavelength range for SPCL. Once the optimum thickness of the metal thin film is determined, additional Fresnel reflectivity curves are calculated for light at various wavelengths. Typically, a shift in the SPR angle is observed with the change in wavelength because of the wavelength-dependent nature of the complex dielectric function of metals. However, for a range of wavelengths where  $\varepsilon_{\rm m}'/\varepsilon_{\rm m}''$  is constant, one can expect the SPR angle will not change (fixed angle) with respect to wavelength of light. In this regard, as an example Fresnel calculations for iron thin films, which predict a fixed SPR angle, are presented. Figure

<sup>(23)</sup> Aslan, K.; Malyn, S. N.; Zhang, Y.; Geddes, C. D. J. Appl. Phys. 2008, 103 084307.



Figure 9. Penetration depth for metal thin films. Plot of calculated electric field intensity (Ez<sup>2</sup>) for penetration depths of the evanescent field at various wavelengths above (A) an 15 nm iron thin film (B) a 50 nm gold thin film and (C) several metals at 620 nm, using three-phase (prism/metal/water) Fresnel calculations.

6 shows that the reflectivity curves for iron thin films in the wavelength range of 496–886 nm (*p*-polarized light) are very similar and the SPR angle does not vary within the 496–886 nm wavelength range (Figure 6-inset). The SPR angle (concomitantly the SPCL angle) occurs at a fixed angle of 60°. It is important to note that the SPR angle is different at wavelengths outside the wavelength range of 496–886 nm (data not shown). On the other hand, at the SPR angle the intensity of reflected *s*-polarized light decreases slightly as the wavelength of light is increased. Iron thin films can be used in SPCL applications in the 496–886 nm wavelength range without changing the angle of observation.

Figure 7 shows that the reflectivity curves for gold thin films in the wavelength range of 496–886 nm (*p*-polarized light) are very different and the SPR angle shifts to lower angles as the wavelength of light is increased. For a *p*-polarized light at 496 nm the reflectivity curve for gold thin films is broad and gets narrower for *p*-polarized light >600 nm (Figure 7-inset). The SPR angle occurs at 54° for *p*-polarized light at 496 nm and shifts to ≈43° at 886 nm. The reflectivity values for *s*-polarized light >600 nm are >0.9, which indicates that the interference from *s*-polarized light at these wavelengths are minimal. Subsequently, gold thin films are an ideal choice for SPCL applications which utilize luminescent species emitting >600 nm, while changing the observation angle according to the results of Fresnel calculations.

In all applications of SPR and SPCL, additional layers in the form of biomolecules, polymers, and so on are always present on top of the metal thin films. In this regard, one has to account for the effect of these overlayers on the SPR angle. For a typical immunoassay constructed on metal thin film the thickness of the additional overlayer can be  $\approx$ 30 nm, which can cause a shift in the SPR (and SPCL) angle. To simulate the presence of overlayers on metal thin films, Fresnel calculations for light at 590 nm are carried out for iron and gold thin film with the addition of a routinely used polymer (poly(vinyl alcohol), PVA). Figure 8A shows that the Fresnel reflectivity curves for iron thin films change slightly. For iron thin films the SPR angle shifts from 60° for a bare surface to a fixed angle of 68° for a surface with 5-30 nm thick overlayer of PVA. That is, one can construct a variety of bioassays on iron films and collect the desired data (kinetic or end-point) at a fixed observation angle of 68° without further adjusting the observation angle. It is interesting to note that the reflectivity curve for s-polarized light does not change with the addition of overlayers, which implies constant background intensity. On the other hand, a significant change in reflectivity curves for gold thin films in the presence of additional overlayers is predicted (Figure 8B). With the addition of PVA overlayers the SPR angle is predicted to shift from 45 to 55°. That is, one has to carefully account for the change in SPR (and SPCL) angle and make necessary adjustments to the observation angle for different bioassays. SPCL data collected during a kinetic or end-point measurement will significantly depend on the addition of biomolecules, which can complicate the overall assessment of data. Similar to iron thin films, the reflectivity curve for s-polarized light does not change with the addition of overlayers on top of gold thin films, which again implies constant background intensity. It is also important to comment on the stability of the metal films, especially under the conditions of biosensing applications. Gold thin films are well-known for their durability under all biosensing conditions, even under acidic conditions that is used to regenerate the surface of the thin films. For the remainder of the metal thin films, an overlayer of  $SiO_x$  can be deposited onto metal thin films using standard laboratory techniques to protect the surface of the metal from chemical degradation.<sup>13</sup>

As briefly discussed in the Theoretical Considerations section light impinging upon on a metallic thin film propagates as an evanescent wave along the metal thin film/dielectric interface (xdirection).<sup>19</sup> This evanescent wave has an amplitude perpendicular to the metal thin film/dielectric interface, which decays exponentially in the z-direction.<sup>19</sup> The penetration depth of the evanescent wave into the dielectric is in the order of several hundred nanometers and provides the opportunity for the selective excitation of luminescent species in close-proximity to the metal thin film.<sup>10</sup> Since the dielectric function of metals differ from one another and is also dependent on the wavelength of light, it is important to study the penetration depth of light with respect to wavelength and the metal type. In this regard, the value for the *z*-component of the electric field  $(E_z^2)$  that occurs at the SPR angle is normalized with respect to the highest value (z = 0)and plotted against the thickness (depth) above the metal. Figure 9A,B shows the penetration depths for light at several wavelengths into the iron and gold thin films. For iron thin films, the evanescent field dissipates exponentially into the dielectric and the metal and is dependent on the wavelength of light. For longer wavelength of light, the evanescent wave becomes more intense at distances between 0-100 nm. For example, for light at 620 nm,  $\approx$ 30% of the electric field intensity is retained 100 nm above the iron surface, while  $\approx$ 40% of the electric field intensity is retained at the same distance. As compared to iron thin films, the intensity of the evanescent wave dissipates significantly more at the same distances above the gold thin films. Figure 9C shows the comparison of the penetration depth of light at 620 nm for nickel, iron, silver, and gold thin films. The evanescent field for light at 620 nm can retain 40% of its original intensity 500 nm above nickel thin films as compared to 20% for iron thin films and 1% for silver and gold thin films. There are several implications for these predictions, including the collection of more light from luminescent species present above nickel thin films, which is especially attractive for the detection of whole-cells, viruses, bacteria and other organisms.

One also has to consider the cost of the metals listed in Table 1 for SPCL applications since the metals significantly differ in the cost of preparation of thin films. For example, rhodium and platinum are the most expensive among the metals. One can employ the relatively inexpensive nickel thin films as an alternative to rhodium. Both rhodium and nickel thin films are predicted to

work in the same spectral regions. Similarly, copper and iron thin films can be employed as an alternative to gold thin films.

### CONCLUSIONS

A generic procedure, based on theoretical Fresnel calculations, for the selection of a metal thin film to be employed in applications of surface plasmon luminescence (SPCL) is presented. Theoretical considerations for SPCL and surface plasmon resonance, which is the basis for SPCL phenomenon, were briefly discussed. Eleven different metals were predicted to potentially cover a wide spectral range from 276 to 1500 nm in SPCL applications. Chromium, aluminum, palladium, and zinc are predicted to find use in the UV and visible spectral ranges. Nickel and rhodium can be used in a broad spectral range, extending from UV to the IR. Silver, gold, iron, and copper were employed in the visible spectral range. Only platinum can be used in the near-IR and IR spectral regions. In addition, the procedure described for the appropriate selection of optimum parameters for metal thin films were demonstrated with iron and gold thin films. The effect of the presence of overlayers on metal films was also studied. The observation angle for SPCL from all metal thin films is predicted to shift with the addition of overlayers, except for iron thin films, which is expected to show a fixed and broad observation angle. The penetration depth of light above metals films was also studied. It was calculated that the evanescent field for light at 620 nm can retain 40% of its original intensity 500 nm above nickel thin films as compared to 20% for iron thin films and 1% for silver and gold thin films, respectively.

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## SUPPORTING INFORMATION AVAILABLE

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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