



Simulation of surface plasmon resonance of Au–WO_{3-x} and Ag–WO_{3-x} nanocomposite films

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ABSTRACT

Surface plasmon resonance (SPR) has been efficiently employed for chemical- and bio-sensing in numerous fields such as molecular biology, medicine, biotechnology, drug and food monitoring, and environmental monitoring. Nanocomposite thin films formed by noble metal nanoparticles embedded in a dielectric matrix show attractive SPR phenomenon due to collective excitations of conduction electrons in metal nanoparticles when photons are coupled to the metal particle–dielectric interface. In this paper, the SPR responses of Au–WO_{3-x} and Ag–WO_{3-x} nanocomposite films with either stoichiometric ($x=0$) and non-stoichiometric ($x>0$) structures were simulated using effective medium theory and Macleod's general characteristic matrices method for various metal percentages and film thicknesses in the Kretschmann configuration at the wavelength of 632.8 nm. Our simulation results predicted that the most suitable Au percentage and film thickness when using non-stoichiometric Au–WO_{3-x} films for SPR gas sensing were 60–80 vol.% of Au with 30–50 nm thickness, while for stoichiometric Au–WO_{3-x} films, Au percentage higher than 40% will lead to a narrow SPR dip for high resolution SPR gas sensing. For Ag–WO_{3-x} nanocomposite films, higher metal percentage and thinner thickness are required to achieve similar sharpness of the SPR dips as that for Au–WO_{3-x} composite films. Our results indicated that the Au–WO_{3-x} and Ag–WO_{3-x} nanocomposite thin films with 40–80% metal fractions and film thickness of 30–50 nm are applicable for optical gas sensing.

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1. Introduction

Surface plasmons [1,2] are surface electromagnetic waves that propagate to and parallel along with a metal/dielectric interface. To excite surface plasmons in a resonant manner, a visible or infrared light beam is typically used to illuminate the metal layer from a glass prism in either Otto [3] or Kretschmann and Raether [4] configurations. Since the surface plasmon waves (SPW) are excited on the boundary of the metal layer, they are very sensitive to any change in the vicinity, such as the adsorption of molecules to the metal surface. It can therefore be used for the detection of molecular adsorption. The materials used for supporting SPW must have free conduction band electrons capable of resonating with the incoming light at a suitable wavelength, e.g., 632.8 nm (1.9593 eV) (He–Ne laser). Metals that satisfy this requirement include Ag, Au, Ti, Cr, Cu, Al, and In. Among all these metals, silver and gold are commonly

used to support surface plasmons, since other metals are either too reactive or too expensive or too susceptible to oxidation.

If biopolymer molecules are immobilized on the surface of the metal layer, the optical reflectivity of the metal layer changes very sensitively with the presence of any binding between the immobilized biomolecules and solution-phase interactants that are in contact with the metal layer; therefore surface plasmon resonance (SPR) can be used for probing the interactions of a variety of biomolecules with various ligands, biopolymers, and membranes [5]. When SPR is considered for the detection of gas molecules [6], it requires that the gas molecules can interact with the metal layer and cause the change in its optical property. Noble metals such as Au and Ag are not reactive to many gases; therefore they cannot be directly used for gas sensing with a typical SPR design. A highly reactive metal oxide [7] or polymer thin film is usually coated on the gold surface, the reaction between gases and the sensing metal oxide or polymer layer induces changes in the optical property of the metal layer, which forms the basis of SPR gas sensing.

Nanocomposite [8] thin films formed by noble metal nanoparticles such as Au embedded in a dielectric matrix can also show SPR response due to collective excitations of conduction electrons

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in metal nanoparticles when photons are coupled to the metal particle–dielectric interface. If a highly reactive metal oxide such as SnO₂ [9] and WO₃ [10] were used as the dielectric matrix in the metal–dielectric nanocomposite, we expect that the interaction between the metal oxide and gas molecules through either chemical reaction or physical adsorption may induce significant change in optical reflectivity of the composite film therefore offers the possibility to measure small concentrations of gases.

In this article, SPR responses of Au–WO_{3–x} and Ag–WO_{3–x} nanocomposite films when stimulated by a He–Ne laser light (632.8 nm) in the Kretschmann configuration were simulated. The dielectric constants of Au–WO_{3–x} and Ag–WO_{3–x} nanocomposite thin films were first determined using the effective medium theory, and then the SPR responses of the nanocomposite film was simulated for various film thicknesses and metal volume fractions in the Kretschmann configuration using Macleod's general characteristic matrices method. WO_{3–x} [11] was selected as the dielectric matrix because it is one of the most interesting materials in the field of gas sensors and shows good sensitivity towards the detection of a number of gases such as NO, CO, H₂S, and O₃. Au or Ag was selected as the metal to carry the SPW as they are the most common SPR materials [2]. Addition of small amount of Au or Ag into WO_{3–x} could also improve the gas detection sensitivity and selectivity as the Au or Ag nanoparticles are good catalysts [9], [10]. Our numerical simulation results provide vital information for future designs of SPR gas sensors based on metal–dielectric nanocomposite films.

2. Theory

The effective medium theory (EMT) [12] is employed to obtain the effective dielectric constant of the Au–WO_{3–x} and Ag–WO_{3–x} nanocomposite, which is the first step to calculate the SPR response of the nanocomposites. The most commonly used SPR setup is the Kretschmann SPR configuration [1,4], which consists of a glass prism, a thin conducting film attached to the prism, and the ambient dielectric material. The SPR response is generally characterized by the reflectance of the *p*-polarized incident beam, i.e., R_p , which can be obtained from either direct calculation [13] or Macleod's general characteristic matrices method [14].

2.1. Effective medium theory

The microstructures of inhomogeneous materials such as metal–dielectric composites can be classified roughly into two types, the separated-grain structure in which the metal particles are dispersed in a continuous host of dielectric medium, and the aggregate structure in which constitutes metal and dielectric particles mix randomly to form a space-filling mixture. Maxwell–Garnett effective medium theory was developed for the optical property analysis of the separated-grain structure, while Bruggeman theory was for the aggregated structure [12]. If a composite material is composed of two mediums with dielectric constant ϵ_1 and ϵ_2 , respectively, and the volume-filling factor of medium 1 is f_1 , then the effective permittivity of the composite is

$$\epsilon_{\text{eff}} = \epsilon_2 \frac{\epsilon_1 + 2\epsilon_2 + 2f_1(\epsilon_1 - \epsilon_2)}{\epsilon_1 + 2\epsilon_2 - f_1(\epsilon_1 - \epsilon_2)} \quad (1)$$

from Maxwell–Garnett formulation for separated-grain structure and

$$f_1 \frac{\epsilon_1 - \epsilon_{\text{eff}}}{\epsilon_1 + 2\epsilon_{\text{eff}}} + (1 - f_1) \frac{\epsilon_2 - \epsilon_{\text{eff}}}{\epsilon_2 + 2\epsilon_{\text{eff}}} = 0 \quad (2)$$

from Bruggeman theory for more dense (interconnected) mixtures of materials.

Neither Maxwell–Garnett nor Bruggeman formulations above explicitly reveal the dependence of the effective dielectric constant on grain sizes and shapes, and their applicability is restricted to situation when grain size is much smaller than the wavelength of the incident radiation at which Rayleigh theory of scattering is applicable. Under such conditions, the particles scatter radiation weakly and essentially behave as electric dipoles under the action of the electromagnetic fields. However, when grain size becomes comparable to the wavelength of the incident radiation, metallic particles may produce a considerable amount of multiple scattering. In addition, Maxwell–Garnett theory which assumes metallic particles are spherical cannot explain the observed dielectric function anisotropy for composite with large ellipsoidal particles. Numerous models have been developed to account for larger particles sizes [15] and for metal concentrations close to percolation conditions [16,17].

2.2. Surface plasmon resonance

When using a visible or infrared light beam to excite surface plasma waves in the Kretschmann configuration, the light is shone on the wall of a prism and totally reflected. An evanescent wave penetrates through the metal film that is evaporated onto the prism to excite and interact with the plasma waves on the metal surface. Under certain conditions, free electrons respond collectively by oscillating in resonance with the incident light wave to generate SPR. The SPR response is generally characterized by the reflectance of the *p*-polarized incident beam, i.e., R_p , which can be calculated as [13,18]

$$R_p = \left| \frac{r_{\text{pm}} + r_{\text{md}} \exp(2ik_{\text{zm}}d_{\text{m}})}{1 + r_{\text{pm}}r_{\text{md}} \exp(2ik_{\text{zm}}d_{\text{m}})} \right|^2 \quad (3)$$

with $r_{\text{pm}} = (\epsilon_{\text{p}}k_{\text{zm}} - \epsilon_{\text{m}}k_{\text{zp}}) / (\epsilon_{\text{p}}k_{\text{zm}} + \epsilon_{\text{m}}k_{\text{zp}})$ and $r_{\text{md}} = (\epsilon_{\text{m}}k_{\text{zd}} - \epsilon_{\text{d}}k_{\text{zm}}) / (\epsilon_{\text{m}}k_{\text{zd}} + \epsilon_{\text{d}}k_{\text{zm}}$. Here k is the wavenumber, d the film thickness, and $i = \sqrt{-1}$ is the imaginary symbol. The wavenumbers along *x*- and *z*-directions are $k_x = n_{\text{p}}k_0 \sin\theta_{\text{p}}$ and $k_{zi} = \sqrt{\epsilon_i k_0^2 - k_x^2}$, respectively. The subscripts 0, p, m, and d denote free-space, prism, metal, and dielectric (ambient or embedding material), respectively. The reflectance can be equivalently obtained from Macleod's general characteristic matrices method as in [14].

3. Results and discussion

3.1. Dielectric constant of Au–WO_{3–x} and Ag–WO_{3–x} nanocomposites

Dielectric constant of Au–WO_{3–x} and Ag–WO_{3–x} nanocomposites films was calculated from Eq. (1). The index of refraction, n , and extinction coefficient, k , of Au and Ag used in the calculation were obtained from the CRC Handbook of Chemistry and Physics [19], and other literatures [2,20–23]. The refractive index n and extinction coefficient k for Au are $n = 0.16172$, $k = 3.21182$, and for Ag are $n = 0.27$, $k = 4.18$, [19] at the wavelength of 632.8 nm (1.9593 eV) (i.e. the wavelength of He–Ne laser).

The n and k of WO_{3–x} films used in the calculation were measured from WO_{3–x} films deposited by pulsed laser deposition (PLD) [24]. WO_{3–x} films were deposited in both high vacuum ($<10^{-6}$ Torr) and oxygen (40 mTorr) ambient. The WO_{3–x} films were deposited by ablating a 90 mm diameter rotating WO₃ (99.99% purity, from Super Conductor Materials) in an advanced deposition chamber (PVD Inc., PLD-3000) by means of a pulsed KrF excimer laser ($\lambda = 248$ nm, Lambda Physik, LPX-210i), at a repetition rate of 50 Hz. The laser beam was focused down to a spot size of ~ 4 mm² on the

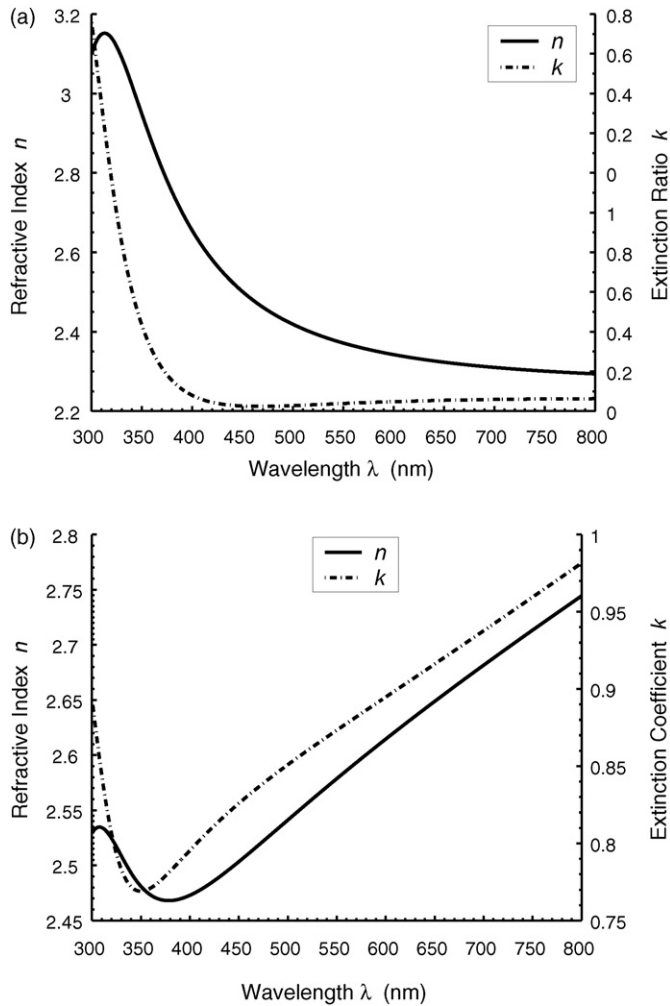


Fig. 1. Optical property (n, k) spectrums for WO_{3-x} thin films fabricated with PLD: (a) in 40 mTorr of oxygen (O_2) with thickness $d = 203.5$ nm; (b) in high vacuum (HV) with thickness $d = 79$ nm.

target surface and the on-target laser beam fluence was adjusted to about $2\text{--}3\text{ J/cm}^2$. An $18\text{ mm} \times 18\text{ mm} \times 1.0\text{ mm}$ rectangular SF10 (from GWC Technologies) glass was used as the substrate for the deposition. The WO_{3-x} films deposited in high vacuum (HV) are non-stoichiometric with oxygen deficiency (e.g. WO_{3-x} , where $x > 0$). It appears as black color with low optical transmittance, while WO_{3-x} films deposited in oxygen ambient have light yellow color and are almost transparent. The optical reflectance spectra of WO_{3-x} films deposited in vacuum and in oxygen were measured with a fiber-optic-based spectrophotometer (SCI FilmTEK3000). Their n and k values were calculated from the reflectance spectra by using appropriate material model to fit the measurement data and the results are shown in Fig. 1. The WO_{3-x} films deposited in oxygen have zero extinction coefficient for wavelengths larger than 400 nm, while films deposited in high vacuum have non-zero extinction coefficient with its value increasing from 0.77 and 0.98 as the wavelength increasing from 400 to 800 nm. The origin of the black coloration of the WO_{3-x} films deposited in vacuum comes from the presence of oxygen vacancies associated with tungsten ions in lower oxidation state than 6^+ expected in WO_3 stoichiometry. This consists with the non-zero extinction coefficient. Both stoichiometric and non-stoichiometric WO_{3-x} films are interesting example for numerical simulation since the chemical stoichiometry of WO_{3-x} thin films is strongly influenced by the presence of

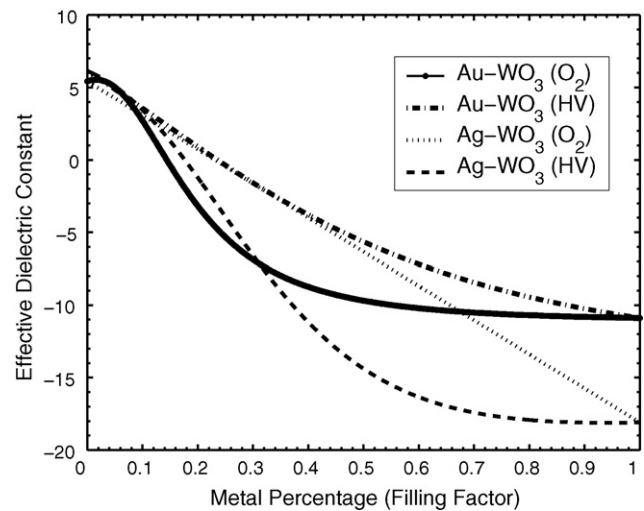


Fig. 2. Dielectric constants of stoichiometric and non-stoichiometric Au-WO_{3-x} and Ag-WO_{3-x} nanocomposite films at 632.8 nm as a function of metal percentage.

either oxidizing or reducing gases when it was used as gas sensors at elevated temperatures. In oxidizing atmosphere, the WO_{3-x} is converted to the stoichiometric WO_3 oxide, while under reducing conditions the oxygen is removed by reaction with the reducing gas species so that WO_3 is converted to non-stoichiometric WO_{3-x} with $x > 0$. From Fig. 1, we determined the n and k values for WO_{3-x} deposited in oxygen (stoichiometric) to be 2.233 and 0.0263 and those for WO_{3-x} deposited in vacuum (non-stoichiometric) are 2.637 and 0.9088, respectively, at the wavelength of 632.8 nm. The (n, k) values together with that of Au and Ag were used to calculate the dielectric constants of Au-WO_{3-x} and Ag-WO_{3-x} nanocomposites films using effective medium theory and the results for real component of the effective dielectric constants ϵ_{eff} are shown in Fig. 2. The ϵ_{eff} is 6.1287 for non-stoichiometric WO_3 , 5.4233 for stoichiometric WO_3 , -10.8698 for Au, and -18.0798 for Ag as shown in Fig. 2. The ϵ_{eff} of the nanocomposite films changes from positive to negative values when the percentage of Au or Ag in the composite films increases. To excite SPR with Kretschmann configuration, ϵ_{eff} of the nanocomposites need to satisfy the conditions $\epsilon_{\text{eff}} < 0$ and $|\epsilon_{\text{eff}}| > \epsilon_d$ [2], where ϵ_d is for the ambient dielectric materials (i.e. gases or aqueous solutions) and is generally greater than 1. Fig. 2 shows that the metal percentage has to be large enough to have sufficiently negative ϵ_{eff} values. On the other hand, too small WO_{3-x} percentage will degrade the performance of the nanocomposite films for optical gas sensing. Considering this trade-off, our discussion on SPR of Au-WO_{3-x} and Ag-WO_{3-x} nanocomposite films below will be focused on metal percentage range between 20 and 80%.

3.2. SPR response of Au-WO_{3-x} and Ag-WO_{3-x} nanocomposites

SPR responses (reflectance vs. angle of incident) of Au-WO_{3-x} and Ag-WO_{3-x} films when stimulated by a He-Ne laser light at the wavelength of 632.8 nm in the Kretschmann configuration were simulated using Eq. (3) and the results are shown in Figs. 3–5. In Fig. 3, we show the SPR response of non-stoichiometric Au-WO_{3-x} films with various Au volume percentages (filling factors) and film thicknesses. The gold percentages are varied from 20 to 80% and thicknesses are from 20 to 60 nm. When Au% equals to 20%, the reflectance approaches zero at an incident angle of 61° if the thickness of the film is 40 nm. Film thickness larger or smaller than 40 nm cannot achieve zero reflectance at any angle of incidence indicating that 40 nm is the optimized thickness to achieve the best SPR

response for Au-WO_{3-x} film with 20% Au. However, its SPR dip is too broad to achieve higher-resolution SPR gas sensing. When Au volume percentage increases, the SPR dips become narrower. For those high Au percentage films, the zero reflectance occurs at the film thickness around 30–40 nm at an incident angle at 45–46°. Although the SPR dips for Au-WO_{3-x} film with 40% Au are sharper than those of 20% films, they are still too broad to achieve high resolution for gas sensing. Only when the percentages of Au are higher than 60%, the SPR dips are reasonably narrow which warrants its practical applications. When Au percentage reaches 80%, the SPR is very sharp. Although films with higher percentage of Au give sharper SPR response, they may not be most suitable for SPR gas sensing since the WO_{3-x} is the main component in the composite film to interact with gases and cause the shift of the SP resonance angle. Based on the analysis in Fig. 3, we predicted that the most suitable Au percentage and film thickness when using Au-WO_{3-x} films for SPR gas sensing should have the Au percentage between 60 and 80% and thickness between 30 and 50 nm.

SPR response for stoichiometric Au-WO_{3-x} is shown in Fig. 4. Very similar to Fig. 3, the SPR dips become sharper as the Au percentage increases. The significant difference between Figs. 3 and 4

is that the SPR responses for stoichiometric Au-WO_{3-x} films are sharper than that of non-stoichiometric films. For the film with Au content as low as 20%, the SPR dip is already reasonably narrow. Stoichiometric Au-WO_{3-x} films with Au percentage higher than 40% will lead to a satisfactory resolution for SPR gas sensing. This is indeed beneficial, since more WO_{3-x} in the composite films will enhance the gas detection. The optimized film thickness for Au percentage less than 40% is 30–40 nm, while for higher Au percentage, the optimized thickness is between 40 and 50 nm.

Similar numerical simulations were also performed for Ag-WO_{3-x} composite films with both non-stoichiometric and stoichiometric WO_{3-x}. SPR responses for 30 nm thick Ag-WO_{3-x} composite films of various Ag percentages are shown in Fig. 5. Similar to Au-WO_{3-x} composite, narrower or sharper SPR dips were found for the nanocomposites with stoichiometric WO_{3-x} comparing to those for non-stoichiometric WO_{3-x}. For Ag-WO_{3-x} with non-stoichiometric WO_{3-x}, narrower SPR dip only occurs for Ag percentage higher than 80%, while for lower Ag percentage SPR dips are very broad which are not suitable for high-resolution SPR sensing. For Ag-WO_{3-x} with stoichiometric WO_{3-x}, however, when Ag percentage reaches 60%, the SPR dip is reasonable narrow indicating

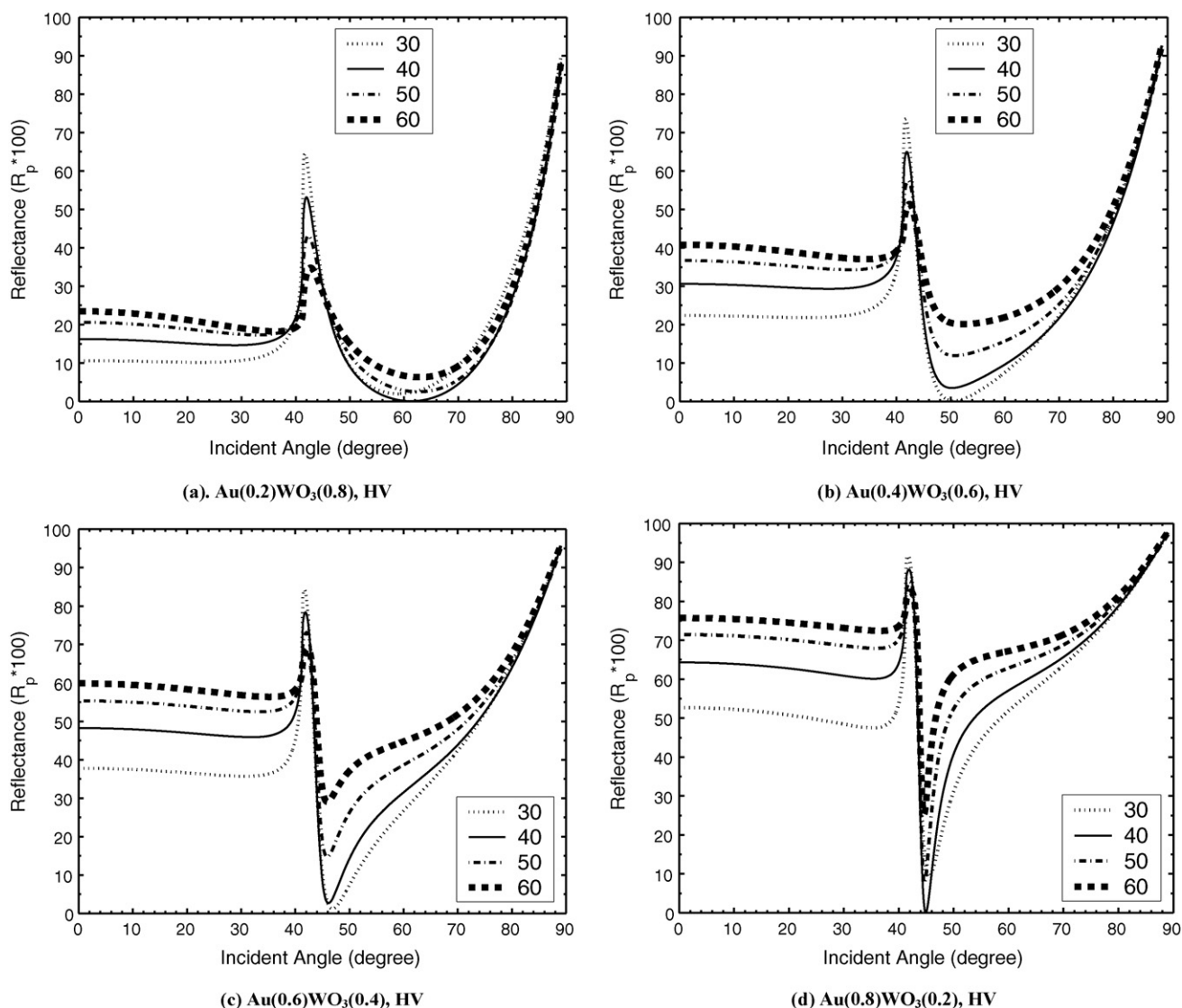


Fig. 3. SPR response of non-stoichiometric Au-WO_{3-x} nanocomposite thin films with various Au percentages and film thicknesses.

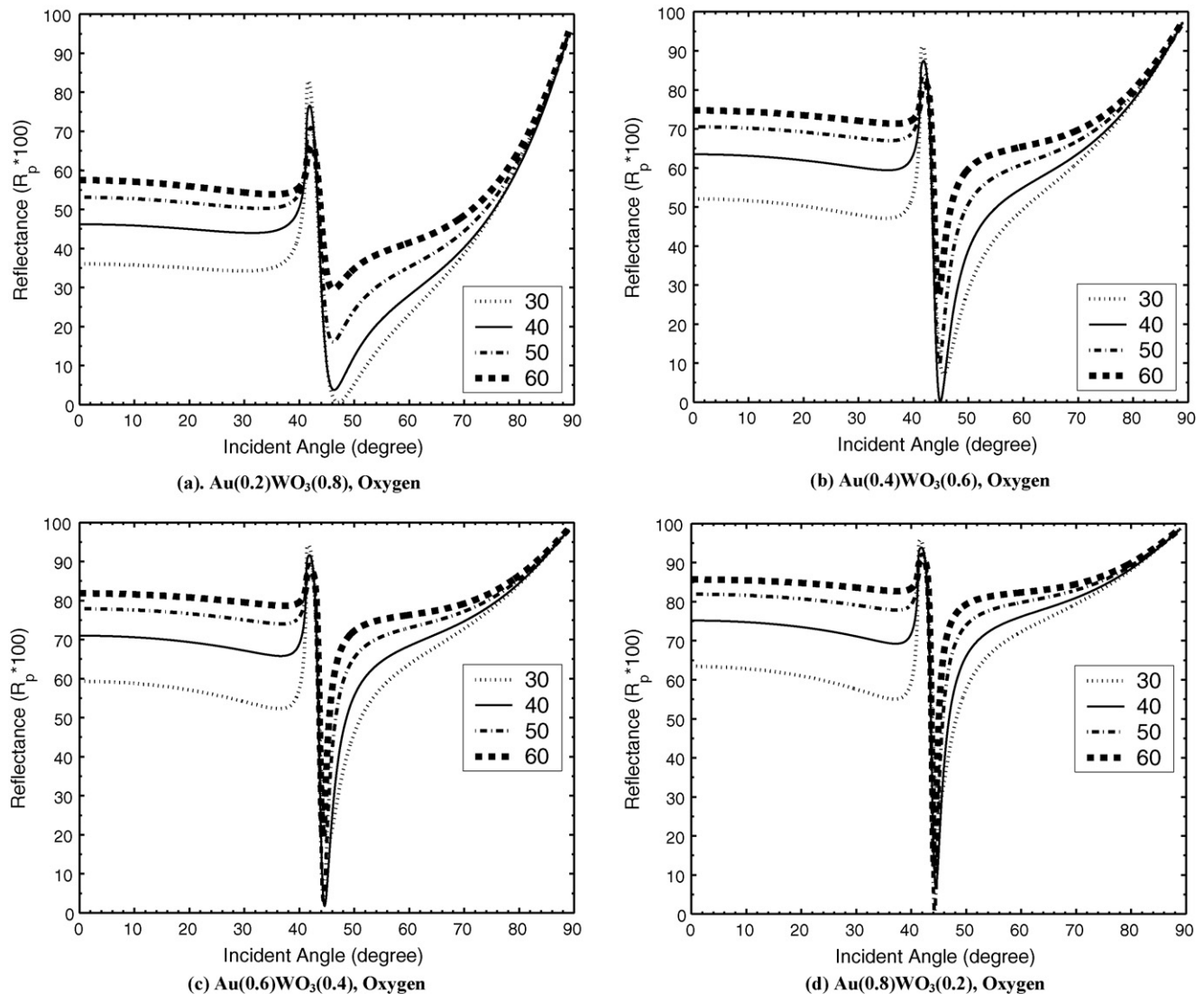


Fig. 4. SPR response of stoichiometric Au-WO_{3-x} nanocomposite thin films with various Au percentages and film thicknesses.

that stoichiometric Ag-WO_{3-x} composite films with Ag percentage higher than 60% are suitable for SPR gas sensing. In comparison with Au-WO_{3-x} composite films, higher metal percentage and thinner thicknesses are needed for Ag-WO_{3-x} composite films to achieve similar sharpness of the SPR dips as for Au-WO_{3-x} composite films. Since Ag is more susceptible to oxidization in air or oxidizing environment, the durability of a thin Ag-WO_{3-x} composite film for the SPR gas sensing may limit its practical applications.

As Maxwell-Garnett theory was developed for the separated-grain structure, it is interesting to see what will be the difference for the aggregate structure where Bruggeman theory is used. To illustrate the difference of the two theories, the SPR responses of 40 nm 80% Au-WO_{3-x} and 30 nm 80% Ag-WO_{3-x} films were simulated using ϵ_{eff} calculated by both theories and their results are compared in Fig. 6. It is clear that the two theories do not agree well with each other. SPR responses predicted by Maxwell-Garnett formula for both composites give much sharper SPR dips than that predicted by Bruggeman theory. The reflectance minimum calculated by Maxwell-Garnett formula approach zero at 42.4° for Au-WO_{3-x} and 42.0° for Ag-WO_{3-x} while those calculated by Bruggeman theory do not reach zero and its minimum is 42.5° for Au-WO_{3-x} and 43.0° for Ag-WO_{3-x}. A more comprehensive simulation using

Bruggeman theory for various Au and Ag percentages in Au-WO_{3-x} and Ag-WO_{3-x} composites together with a comparison of the simulation results with experimental measurements for PLD prepared composite films will be given in our future communication.

It is known that the chemical stoichiometry of WO_{3-x} thin films when used as gas sensors at elevated temperatures is strongly influenced by the presence of oxidizing or reducing gases. In oxidizing atmosphere, the WO_{3-x} is approaching to the stoichiometric WO₃ oxide structure (i.e. $x \rightarrow 0$) showing a high electrical resistance. Under reducing conditions, the oxygen is removed by reaction with the reducing gas species and the x in WO_{3-x} increases: as a result, the oxide layer electrical resistance decreases. Similar to the electrical conduction, the optical properties (i.e. n and k) of stoichiometric WO₃ and non-stoichiometric WO_{3-x} (with $x > 0$) are significantly different as shown in Fig. 1. WO₃ have zero k at wavelength λ larger than 400 nm while WO_{3-x} (with $x > 0$) has non-zero k at $\lambda > 400$ nm indicating a strong absorption of light. The significant difference in n and k of stoichiometric and non-stoichiometric WO_{3-x} results in distinguishable SPR spectra. To use Au-WO_{3-x} and Ag-WO_{3-x} composite films as SPR gas sensors, it is very important to understand how SPR response will change if WO₃ is converted to WO_{3-x} (with $x > 0$) under reducing gases and vice versa under oxidizing

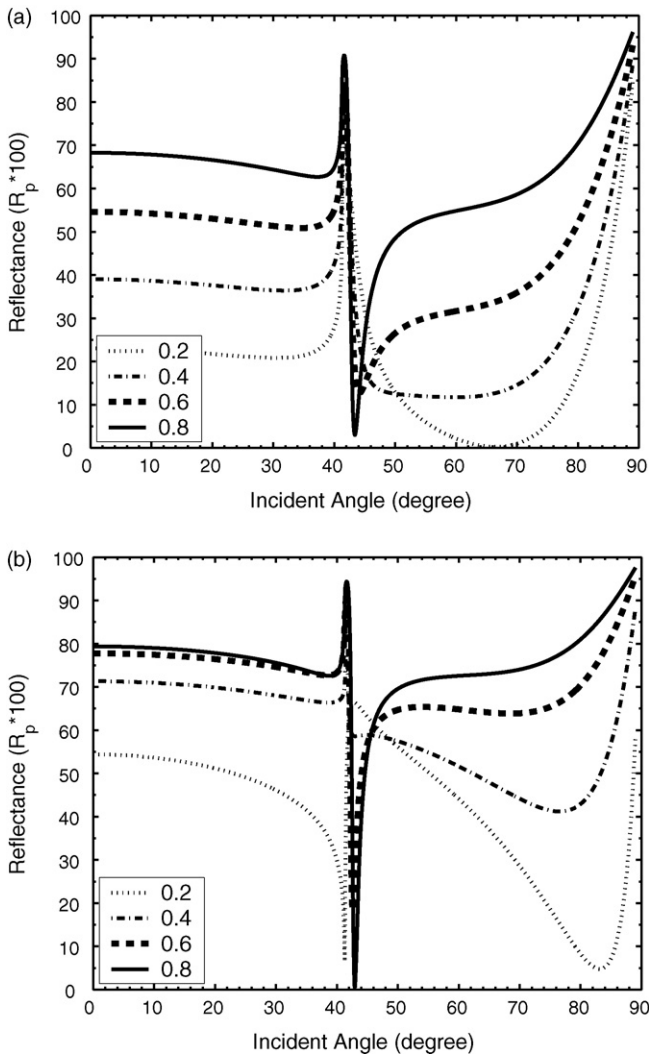


Fig. 5. SPR response of 30 nm Ag-WO_{3-x} nanocomposite thin films with various Ag percentages: (a) with WO_{3-x} fabricated in high vacuum PLD chamber (non-stoichiometric films); (b) WO_{3-x} fabricated in PLD chamber with oxygen (stoichiometric films).

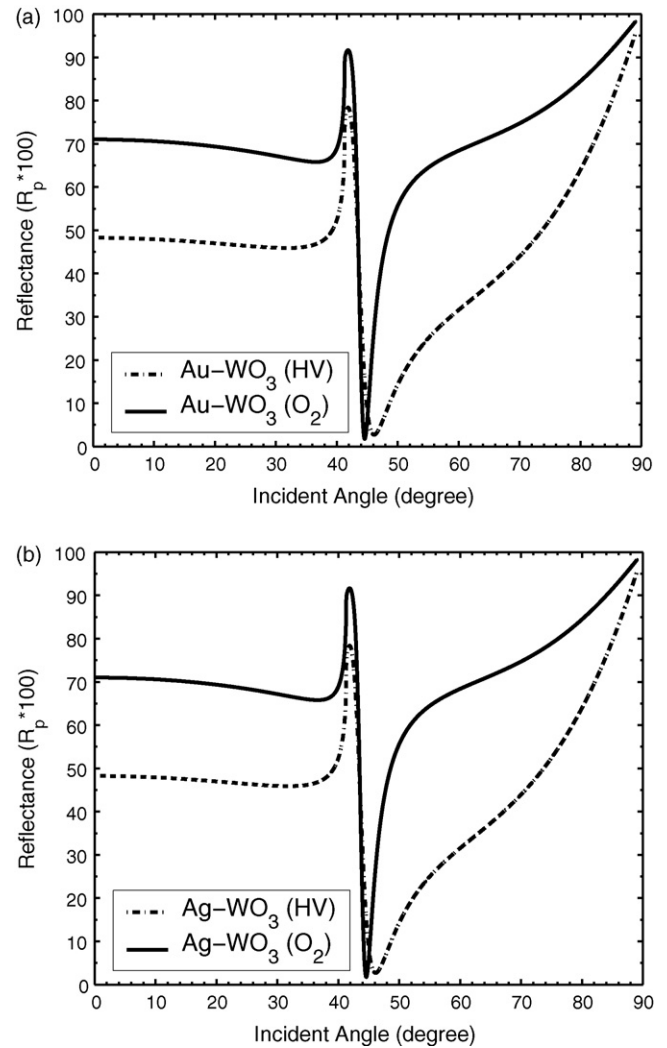


Fig. 7. SPR response of non-stoichiometric and stoichiometric (a) Au-WO_{3-x} films of 40 nm thickness and 60% of Au and (b) Ag-WO_{3-x} of 30 nm thickness and 60% of Ag.

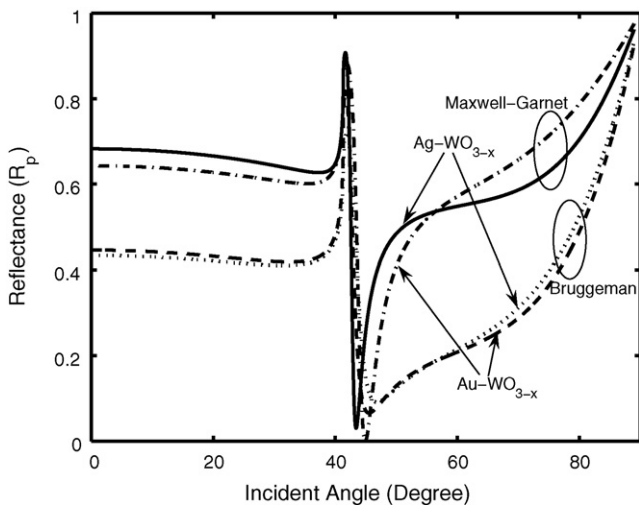


Fig. 6. Comparison of Maxwell-Garnett and Bruggeman formulas for calculating the SPR responses of a 40 nm 80% Au-WO_{3-x} film and a 30 nm 80% Ag-WO_{3-x} film.

gases. Fig. 6 shows the SPR response of Au-WO_{3-x} and Ag-WO_{3-x} composite films with both non-stoichiometric and stoichiometric WO_{3-x}. The film thickness for Au-WO_{3-x} is 40 nm with 60% Au content, while for Ag-WO_{3-x} films, it is 30-nm thick and 60% Ag. Fig. 7 clearly shows that nanocomposite films with non-stoichiometric and stoichiometric WO_{3-x} are significantly different in SPR spectra. The resonance angle shifts from 44.5° to 46.0° and the SPR dips become broadened when WO₃ becomes WO_{3-x} (with $x > 0$). When Au-WO_{3-x} or Ag-WO_{3-x} composite films are used for gas sensing, it is expected that the SP resonance angle will increase if the composite films are exposed to reducing gas species, and the extent of the angle increase will depend on the concentration of the gas and the temperatures of composite films. If the detection angle of a photo detector is fixed at 44.5° and the reflectance is measured, we expect that the reflectance will increase when the composite films are exposed to the reducing gas species and visa versa. Fig. 7 explains the fundamental of how to use Au-WO_{3-x} or Ag-WO_{3-x} composite films for SPR gas sensors.

As gas sensing using WO_{3-x} thin films normally operates at elevated temperatures, it is very important to understand the temperature dependent SPR responses of Au-WO_{3-x} or Ag-WO_{3-x} composite films. The temperature dependence of metallic components ϵ_1 and dielectric component ϵ_2 determines the temperature

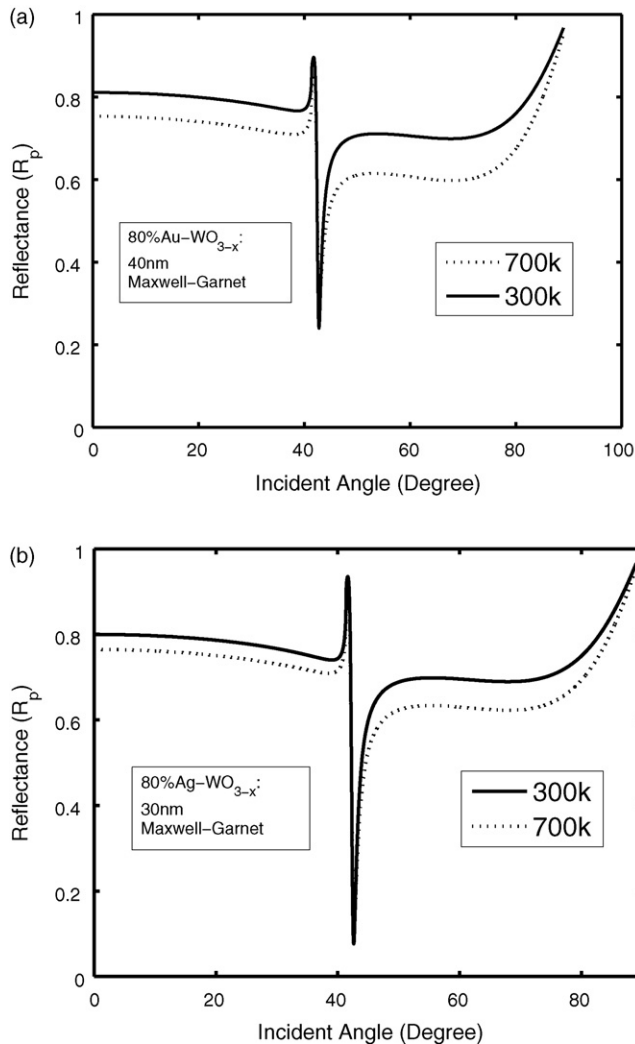


Fig. 8. SPR responses of a 40-nm 80% Au-WO_{3-x} (a) and a 30-nm 80% Ag-WO_{3-x} (b) films at 27 and 427 °C with ϵ_{eff} (690 nm) calculated from Maxwell-Garnett theory.

dependence of the composite ϵ_{eff} and thereafter the SPR response (see Eqs. (1) and (2)). For the metallic component ϵ_1 , a Drude model is often used to determine the temperature dependence [25]. For example, at 690 nm radiation the index of refraction, n , of both Au and Ag increases significantly with the increase in temperatures, while their extension coefficients, k , are almost independent of temperatures, for a large temperature range up to 1000 °C. For the dielectric component ϵ_2 , in general, it is known to have as negligible temperature dependence [26]. For example [27], the n and k of thermally evaporated WO₃ thin films at 22 °C are 2.06123 and 0.00869, respectively, while at 180 °C, they only slightly change to 2.05810 and 0.00918, respectively.

To better understand the temperature dependent SPR response of Au-WO_{3-x} and Ag-WO_{3-x} composites, we took the n and k data from Ref. [25] for both Au and Ag at 27 and 427 °C at 690 nm (data for 632.8 nm is not available in this reference). The n and k for Au are 0.1468, 4.64 at 27 °C, and 0.3631, 4.64 at 427 °C, respectively. For Ag, they are 0.073, 5.012 at 27 °C, and 0.204, 5.012 at 427 °C. The n , k data for WO_{3-x} from was taken from Fig. 1(b). They are 2.675 and 0.935 at 690 nm and assumed to be temperature independent. The simulated SPR responses using Maxwell-Garnett theory are shown in Fig. 8. It is clearly seen that the resonance angles of both Au-WO_{3-x} and Ag-WO_{3-x} do not change with temperatures; however, their reflectance decreases at all the angles of incident.

4. Conclusions

Surface plasmon resonance responses of Au-WO_{3-x} and Ag-WO_{3-x} nanocomposite films were simulated for various metal percentages and film thicknesses in the Kretschmann configuration at the wavelength of 632.8 nm. The optical properties (e.g. n and k) of Au, Ag, and WO_{3-x} were used in Maxwell-Garnett formulation for the calculation of dielectric constant of the composite films. The SPR response of composite films was simulated using Macleod's general characteristic matrices method. Numerical simulation was performed for Au-WO_{3-x} and Ag-WO_{3-x} films with WO_{3-x} of both non-stoichiometric ($x > 0$) and stoichiometric ($x = 0$) structures, deposited by PLD in high vacuum (HV) and in 40 mTorr of O₂, respectively. SPR dips for stoichiometric Au-WO_{3-x} or Ag-WO_{3-x} films are sharper than those of non-stoichiometric Au-WO_{3-x} or Ag-WO_{3-x} films. Our simulation results predicted that the most suitable Au percentage and film thickness when using non-stoichiometric Au-WO_{3-x} films for SPR gas sensing are 60–80 vol.% of Au with 30–50 nm thickness, while for stoichiometric Au-WO_{3-x} films, Au percentage higher than 40% would lead to a satisfactory resolution for SPR gas sensing. As for Ag-WO_{3-x} composite films, higher metal percentage and thinner thickness are required to achieve similar sharpness of the SPR dips. When Au-WO_{3-x} or Ag-WO_{3-x} composite films are used for gas sensing, it is expected that the SP resonance angle will increase if the composite films are exposed to reducing gas species and visa versa for oxidizing gas species. The extent of the SPR angle change will depend on the concentration of the gas.

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