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Performances of Surface Plasmon Sensors using Transition Metal Nitrides

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***Abstract*—We are numerically investigating the performances of surface plasmon sensors based on transition metal nitrides instead of noble metals, such as silver and gold. These alternative metal presents improved thermal and mechanical properties that support the design of better sensors for harsh environment. The result show that titanium nitride and zirconium nitride are viable alternative to silver as the sensitivity of sensors using these metals is better than sensors using silver.**

Keywords—Transition metal nitrides, SPR sensors

I. INTRODUCTION

Surface plasmon resonance (SPR) has been understood for some decades, but the emergence of nano-technologically derived materials has significantly reinvigorated this field. Since its discovery, SPR has become an almost indispensable diagnostic technique for probing a broad range of physical, chemical and biological measurands [1-2]. Essential to SPR is the excitation of free conducting electrons (or plasmons) at the interface between two materials, typically one a dielectric, the other a metal with an abundance of conduction electrons [1]. Although, most conductive materials support surface plasmon (SP), noble metals such as gold and silver are traditionally employed in SPR as their resonances are situated in the visible and thus allow SP excitation by standard optical sources.

Sensor technologies have seen a recent exponential growth two key areas: SPR and optical fibre sensors. These have tended to address different market sectors but "lab-on-fibre" technologies promise to combine the best aspects of both [3]. One constraint on current SPR technology arises from material limitations. Gold and silver exhibit high absorption leading to large losses (and short SPR propagation length) while glass waveguide structures cannot be employed much beyond 1273°K. Further, metal-based sensors tend to degrade in the presence of corrosive chemicals. Another major problem is the relatively poor adhesion of metallic components to the waveguides or substrates. Thus, traditional SPR materials are insufficiently robust for use in harsh environment sensing. Recently, a new class of SPR materials has been reported which exhibit SP behaviours with relatively low losses and extended operating wavelengths compared to noble metals. These are based on transition metal oxides and nitrides, and are materials having high melting temperatures and chemical stability at temperatures above 2000°K [4-5]. These materials can facilitate the design of devices with a spectral window extending beyond that of conventional SPR materials [6] and capable of operating under a broader, more extreme range of environmental conditions [4]. As an example, titanium nitride (TiN) deposited on a sapphire substrate have demonstrated resonances at two wavelengths in the near-IR (900 nm and 1000 nm) [7].

In this paper, we are investigating, from a numerical point of view, the performances of a SPR sensor using transition metal nitrides, titanium nitride (TiN) and zirconium nitride (ZrN), deposited on sapphire (Al_2O_3; m.p. 2323°K). The aim is to evaluate how the performances of such sensors, in particular the sensitivity, compare with SPR sensors using noble metals. For this study, possible issues with control of deposition, quality of adhesion and effect of temperature are not considered as they would be a problem only if the sensor can present a good sensitivity.

II. SPR SENSOR AND THEORY

A. Definition and Sensor Structure

A plasmon corresponds to an oscillation of free electrons in a metal or metal-like materials. Two types of plasmon can exist in a metal: bulk plasmon and surface plasmon. In the former, the oscillation involves the free electrons in the entire metal layer. While, in the latter, the oscillation is limited to the surface of the metal, i.e. the interface between metal and dielectric. Surface plasmons have exhibited high sensitivity to changes in the dielectric property of the dielectric, which has been used to design highly sensitive sensors.

In this paper, we will focus on modelling and simulating the performances of the classic Kretschmann configuration. Figure 1 illustrates this structure where a prism is used to allow phase matching between the incident light and the surface plasmon, thus leading to its excitation.

The structure comprises three different materials: a dielectric prism, a metal layer and the outer dielectric, which is the medium to sense. When the permittivity (or refractive index) of the outer dielectric changes, the condition to have phase matching changes. In turn, it modifies the angle of incidence or the wavelength of the excitation light that matches the surface plasmon propagation vector.

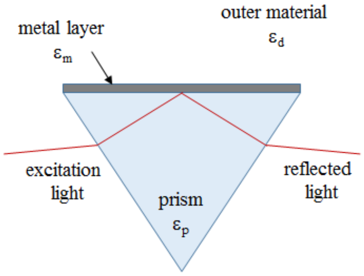

Fig. 1 Kretschmann configuration

In this configuration, the surface plasmon exists at the interface between the metal and the outer material. However, the excitation condition will also depend on the prism material.

B. Theoretical Model

In this section, the key equations to study a surface plasmon-based sensor are summarized, i.e. SPP dispersion and reflectance for TM waves.

In the following paragraphs, the three materials highlighted in section II are modelled by their permittivity, i.e. ε_p for the prism, ε_m for the metal and ε_d for the outer layer. The permittivity of the prism and outer layer can be considered real (imaginary part is null) but the permittivity of the metal is complex, as will be discussed in the next section.

1) SP dispersion: the dispersion of the propagation constant of the SP, noted β, can be expressed as a function of the permittivity of the metal and outer material as follow:

$$\beta = k_0\sqrt{\frac{\varepsilon_m\varepsilon_d}{\varepsilon_m+\varepsilon_d}} \tag{1}$$

Where k_0 is the propagation constant in free space.

2) SP excitation: due to the nature of the SP, only p-polarised wave can excite a SP. The reflection coefficient of the excitation light is expressed by:

$$R^{TM} = \frac{R_{pm}^{TM} + R_{ms}^{TM}e^{i2k_m d}}{1 + R_{pm}^{TM}.R_{ms}^{TM}e^{i2k_m d}} \tag{2}$$

where R_{pm}^{TM} is the reflectance at the interface prism/metal, R_{ms}^{TM} is the reflectance at the metal/outer material interface and k_m is the propagation constant in the metal. Their detailed expression can be found in [8].

III. MATERIAL INFORMATION AND MODELS

A. Prism

For the work in this paper, the prism is considered being made of sapphire. The permittivity of sapphire is modelled based on experimental data for single crystal sapphire produce by one of the authors.

B. Transmission Metal Nitrides

Transition metal nitrides, such as TiN and ZrN, are non-stoichiometric ceramic that can exhibits metal behaviour for some range of wavelength. The metal-like properties, and thus the suitability to be used in SPR sensors, is sensitive to the stoichiometry. We have chosen samples presenting a stoichiometry close to 1.

To model the permittivity of a metal Drude-Lorentz model can be used. Its general formula is:

$$\boldsymbol{\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} + \sum_{k=1}^{m}\frac{A_k^2}{(\omega_{0k}^2 - \omega^2) - i\gamma_k\omega}} \tag{3}$$

where ε_∞ represents the residual polarisation of the atoms, ω_p is the plasma resonant frequency of the free electrons, γ is the scattering rate, A_k is the amplitude of oscillator k, ω_{0k} and γ_k are the resonant frequency and damping of oscillator k.

Due to their use as ceramic and protective layer, thanks to their hardness, TiN and ZrN have been well studied and many papers have been published on their fabrication and optical constants [9-12]. In the present study, we are using [7] for TiN sample (the coefficients of the Drude model are available in [9]) and [12] for ZrN. Finally, to compare the performances with noble metal, one published sample of silver thin film is also considered [13].

C. Comparison of Complex Permittivity

From the Drude-Lorentz model for each of the three samples, the variations of their respective permittivity can be compared to verify the metallic behavior. Figure 2 presents the permittivity of samples of silver, TiN and ZrN as a function of wavelength.

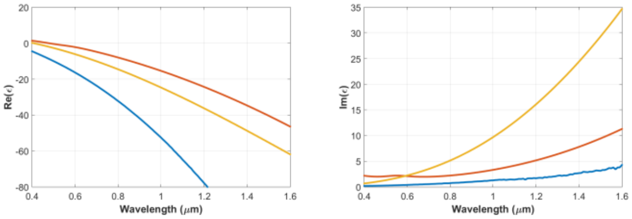

Fig. 2 Real part (left) and imaginary part (right) of the permittivity of silver (blue line), TiN (red line) and ZrN (gold line).

IV. SIMULATION OF SENSOR PERFORMANCES

The reflection coefficient of the excitation light has been computed for the various samples discussed in section III using eq.(2). The two main parameters of interest are the excitation conditions and the sensitivity of the sensor.

A. SPP Excitation

In the sensor configuration selected, the condition of excitation of the SP depends on both the angle of incidence of the light and its wavelength. We will consider that the wavelength is fixed and the focus is on NIR range. The interest for NIR is coming from the commercial availability low-cost devices for telecommunication.

Figure 3 presents the excitation resonance of the SP at the interface metal (silver or ZrN)/outer material for a wavelength of 1μm and for different values of permittivity of the outer material. The response for a silver thin film is as expected: a sharp and deep resonance. However, for the ZrN layer, the resonance is less deep and wider. While showing degraded performances compared to silver, the wider resonance, if moderate, can be beneficial to design a low cost sensor as the detection will not require high angular resolution.

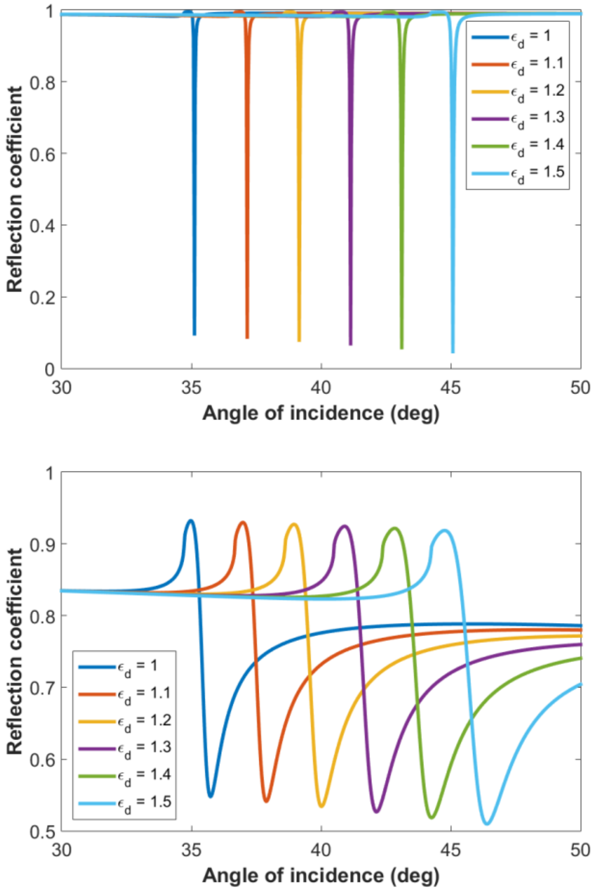

Fig. 3 Excitation of surface plasmon for silver (top) and ZrN (bottom) as a function of angle of incidence for different values of permittivity of the outer material. Excitation wavelength is 1μm and the thickness of metal is 50nm.

For both metal layers, it is clear that the resonance is strongly dependent on the permittivity of the outer dielectric. This effect will be studied in more details in the next paragraph.

B. *Sensor Sensitivity*

Based on the excitation condition as a function of the permittivity of the outer dielectic, it is possible to estimate the sensitivity of the sensor. It is calculated following the formula:

$$S = \frac{\Delta\theta}{\Delta\varepsilon} \tag{4}$$

where Δθ is the variation of angle of incidence at resonance and Δε is the variation of permittivity of the outer material.

Figure 4 shows the sensitivity calculated using eq.(4) and the simulation results for the reflection coefficient for a thin film of thickness 50nm made of silver, TiN or ZrN at two different wavelengths: 800nm and 1.3μm. From the simulation results, it is clear that at these wavelengths the performance of transition metal nitrides is comparable to silver with marginally better sensitivity. Of course, it has to be taken into account that silver should perform better in the visible and not in the NIR. But, if one is interested to design SPR sensor in the NIR for reasons explain earlier, alternative metals could provide at least similar performance to silver.

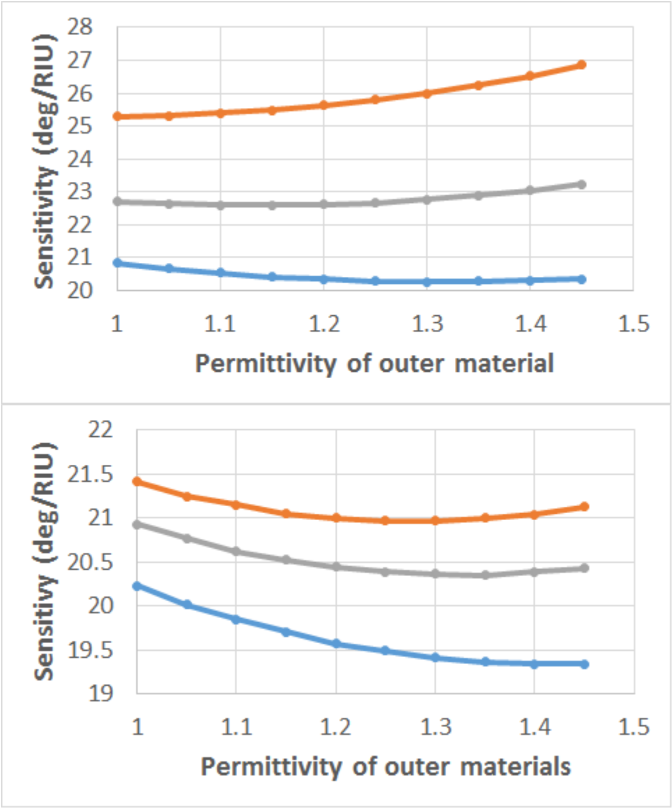

Fig. 4 Sensitivity for silver (blue), TiN (grey), ZrN (orange) as a function of the permittivity of the outer material for two different wavelengths: 800nm (top) and 1.3μm (bottom). Metal layer thickness is 50nm.

V. CONCLUSION

In this paper, we have presented simulation results of a SPR sensor using Kretschmann configuration and transition metal nitride in place of noble metal. The preliminary results shows that TiN and ZrN can be used to design SPR sensor with sensitivity comparable to sensors using silver but with improved thermal and mechanical performances.

One possible drawback is the wider and shallower resonance compared to noble metal. While, it would allow to use a detection with a larger angular resolution, it could make the sensor more sensitive to noise. Further investigations are being carried out to study the impact of the transition metal nitride fabrication method on the overall performance of SPR sensors.

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