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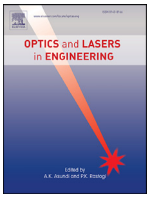

Long-range surface plasmon resonance and its sensing applications: A review

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ABSTRACT

Long-range surface plasmon resonance (LRSPR) sensor, a novel type of surface plasmon resonance (SPR) sensor, is characterized by high sensitivity, high detection accuracy, flexible design, label-free, and real-time analysis. The micron-scale penetration depth of long-range surface plasmon wave (LRSPW) in the analyte makes LRSPR sensor quite suitable for biomacromolecules detection. This paper firstly described the research progress of LRSPR and the sensing characteristics of LRSPR sensor, and then the theoretical fundamentals of LRSPR were introduced. The specific types of LRSPR sensors and applications were detailedly summarized in tabular form, especially the dielectric buffer layers (DBLs) used for the fabrication of LRSPR chips were contrasted. Furthermore, the comparison between conventional SPR (cSPR) and LRSPR was presented, and the future scope of study in LRSPR technology was discussed. LRSPR sensor has drawn more and more attentions because of its excellent sensing performance, and especially the fiber based LRSPR sensor has promising potential in the fields of biochemistry, medicine, food quality inspections, etc.

1. Introduction

Surface plasmon resonance (SPR) is a type of collective oscillation of free charge occurring at the interface between metal and medium [1–6]. According to the sensing structure, SPR sensor can be divided into prism-coupling sensor [7,8], integrated optical waveguide-coupling sensor [9], grating-coupling sensor [10], and fiber-coupling sensor [4,11–13]. Among them, the prism-coupling (prism/metal film/analyte) and fiber-coupling (fiber/metal film/analyte) SPR sensors are most widely used. Compared with conventional biochemical analysis methods, SPR sensing technology is characterized by high sensitivity, label-free, no purification of the analytical sample, strong anti-interference ability, and in-situ dynamic monitoring, making it widely applied in the fields of biochemistry [14], medicine [15], water and food quality inspections [16], environment monitoring [2,17], etc.

In recent years, the rapid development of biotechnology has raised higher requirements for the sensitivity, specificity and advancement of the bioassay methods. Hence, the sensitivity and accuracy of the conventional SPR (cSPR) have gradually been difficult to meet the above requirements well, and the new SPR modes such as long-range SPR (LRSPR) [18], coupled plasmon-waveguide resonance (CPWR) [19], and waveguide-coupled SPR (WCSPR) [19] have been studied. LRSPR, first proposed by Sarid in 1981 [20], is a type of special electromagnetic field mode and also known as long-range surface plasmon polariton (LRSPP) [21]. Compared with other SPR modes, LRSPR is characterized by the dielectric buffer layer (DBL) between the substrate and metal film. Long-range surface plasmon has a weaker confinement within the material layers, allowing it to extend deeper into the analyte. Therefore, the propagation distance of long-range surface plasmon wave (LRSPW) is longer and the electromagnetic field intensity generated by LRSPR is stronger, so that LRSPR has the advantages of higher sensitivity, narrower full width at half minimum (FWHM), and higher detection accuracy compared with cSPR and short-range SPR (SRSPR). Furthermore, the materials of metal films in LRSPR sensing structures has more choice, not only highly reflecting and low absorbing metals (such as Au and Ag) [22] but also highly absorbing metals (such as Ni, Pd, and V) [23] are valid, which extends the applications of LRSPR technology in chemical analysis and other fields.

LRSPR has been paid more attentions so far, and this paper provided a review of LRSPR technology and its sensing applications. This paper began with a section which described the research progress and the sensing characteristics of LRSPR sensor, and then introduced the theoretical fundamentals of LRSPR. In the next section, the specific types of LRSPR sensors and applications as well as the DBLs of LRSPR chips were detailedly summarized and contrasted. Finally, the prospect about the future development directions of LRSPR sensor, especially the application of fiber-based LRSPR sensor was discussed.

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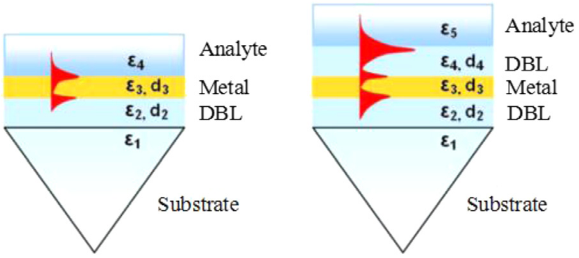


(a) (b)

Fig. 1. Schematic illustration of the sensing structures and electric field distribution for (a) common LRSPR and (b) symmetrical LRSPR (The pictures come from Ref. [25]).

2. The fundamentals of LRSPR

As shown in Fig. 1(a), the structure that excites LRSPR is generally composed by substrate/DBL/metal film/analyte. When a sufficiently thin metal conducting layer is sandwiched by two dielectric layers having the same or similar refractive index (RI), the electromagnetic fields of the surface plasmon polariton that belong to the two interfaces of the metal layer begin to overlap, generating a symmetric electromagnetic field mode and anti-symmetric electromagnetic field mode. The attenuation of the symmetric electromagnetic field is smaller than that of the anti-symmetric electromagnetic field, and the penetration depth in analyte as well as the propagation length along the interface between metal film and analyte of the symmetric electromagnetic field are much larger than that of the anti-symmetric electromagnetic field. Therefore, the symmetric electromagnetic field mode is called LRSPP, while the anti-symmetric electromagnetic field mode is called short-range surface plasmon resonance (SRSPP). Next, the fundamentals of LRSPR will be further introduced by establishing mathematical model.

ε_i, $i = 1, 2, 4$, are the permittivities of substrate, DBL, and analyte, respectively. ε_3 is the complex permittivity of metal, and can be expressed by $\varepsilon_3 = \varepsilon_{r3} + i\varepsilon_{i3}$ [24]. d_i, $i = 2, 3$, are the thickness of DBL and metal film, respectively. In order to facilitate analysis, DBL and analyte are regard as semi-infinite media and the thickness of metal film is mainly considered.

According to the continuity condition of the interface, the dispersion equation of the membrane structure can be derived as [26,27]:

$$\tanh(\alpha_3 d_3) = -\frac{\alpha_3\varepsilon_3(\alpha_4\varepsilon_2 + \alpha_2\varepsilon_4)}{\alpha_3^2\varepsilon_2\varepsilon_4 + \alpha_2\alpha_4\varepsilon_3^2} \tag{1}$$

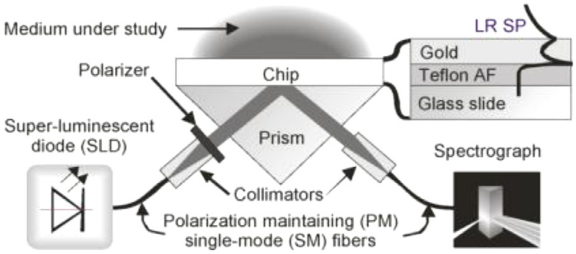


Fig. 3. Schematic representation of the sensor setup (The picture comes from Ref. [29]).

where $\alpha_j^2 = k^2 - k_0^2\varepsilon_j$, $j=1, 2, 3, 4$; $k=k_r - ik_i$, $i = 1, 2, 3, 4$.

When $\varepsilon_2=\varepsilon_4$, and substitute it into Eq. (1). The obtained solutions can be divided into symmetrical mode and antisymmetric mode. For symmetrical mode (i.e. $|\alpha_2\varepsilon_3/\alpha_3\varepsilon_2| < 1$), the dispersion relation can be expressed by [26,27]:

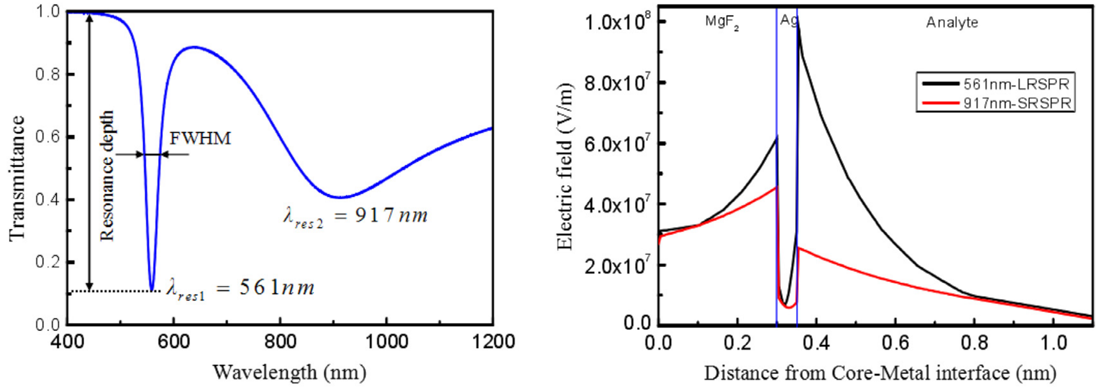
$$\tanh\left(\frac{\alpha_3 d_3}{2}\right) = \frac{-\alpha_2\varepsilon_3}{\alpha_3\varepsilon_2} \tag{2}$$

For antisymmetric mode (i.e. $|\alpha_2\varepsilon_3/\alpha_3\varepsilon_2| > 1$), the dispersion relation can be expressed by [26,27]:

$$\tanh\left(\frac{\alpha_3 d_3}{2}\right) = \frac{-\alpha_3\varepsilon_2}{\alpha_2\varepsilon_3} \tag{3}$$

When d_3 tends to infinity, $\varepsilon_2\alpha_3 + \varepsilon_3\alpha_2=0$ can be derived from Eqs. (2) and (3), indicating that the SPWs propagating along the two interfaces of metal film and whose amplitudes decay exponentially along the direction perpendicular to the interfaces will not overlap in the metal film. When d_3 tends to zero, the two SPWs will overlap, forming symmetric mode and antisymmetric mode. The symmetrical mode is known as LRSPW with small loss, and the antisymmetric mode is known as short-range SPW (SRSPW) with large loss. If $\varepsilon_2 \neq \varepsilon_4$, LRSPR can also be excited in the case of $|\varepsilon_2 - \varepsilon_4| = \Delta << \varepsilon_2, \varepsilon_4$.

As is shown in Fig. 2(a), the wavelength, depth, and FWHM of the resonance dip are important parameters for evaluating the performance of the wavelength modulated LRSPR sensor. The sensitivity of the sensor is defined as $S_\lambda = \delta\lambda_{res}/\delta n$, where $\delta\lambda_{res}$ is the shift of the resonance wavelength and δn generally refers to the change of RI or concentration of aqueous medium. The figure of merit (FOM) of the sensor is defined as FOM $= S_\lambda/FWHM$. The resolution of the sensor is generally calculated as the precision with which SPR feature position can be found, divided by the sensor sensitivity. Note that Fig. 2(a) exhibits two resonance dips, the dip corresponding to the wavelength of 561 nm is narrow and deep and the dip corresponding to the wavelength of 917 nm is broad and



(a) (b)

Fig. 2. Schematic diagram of the (a) LRSPR resonance spectrum and (b) electric field distribution curves of the two resonance dips (The pictures come from Ref. [28]).