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Effects of intermediate dielectric films on multilayer surface plasmon resonance behavior

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Abstract

The effects of intermediate dielectric films on multilayer surface plasmon resonance (SPR) behavior were studied in terms of biosensing applications. Ten simple and complex oxides and fluoride, including $MgF₂$ and MgO , $SiO₂$, $TiO₂$ and complex PZT family dielectric materials, were evaluated. The materials cover a wide range of refractive indices, from 1.19 for the porous silica film to 2.83 for the TiO₂ film. The resonance curves of the multilayer SPR configurations were taken from an angular modulated Kretschmann set-up under a fixed incident wavelength of 543.5 nm. The intermediate dielectric layer has no strong effect on the SPR resonance angle and minimum reflectance at the resonance point. Some intermediate dielectric films, such as MgF₂, porous silica, TiO₂ and PLZT, apparently reduce the width of the resonance curves, resulting in sharper resonance dips. Better performance of the multilayer SPR biosensor incorporating these dielectric films is expected.

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1. Introduction

Surface plasmon resonance (SPR) was first introduced into biosensors by Nylander and Liedberg in 1982 [\[1–3\]](#page--1-0). Since then, many works have been devoted to the development of SPR-based biological sensing. Among a wealth of biosensing techniques, SPR has been recognized as a valuable and standard analytical tool in biophysical and biochemical studies. The technique offers several distinctive features, such as high sensitivity, label-free measurement and real time analysis [\[4\]](#page--1-0).

Surface plasmon waves (SPWs) can be easily excited at the interface between two media with dielectric constants of opposite signs, such as a metal and a dielectric, by an incident electromagnetic light wave. This SPW is confined to a very narrow range of a few nanometers within the

metal surface, while it penetrates tens or hundreds nanometers into the dielectric medium. Surface waves within both the metal and the dielectric evanesce away from the interface. The electric field of the SPW at the interface is very strong and much enhanced in orders of magnitude. Consequently, the SPR technique is very sensitive to environmental changes in the close vicinity of the interface. Any changes in the chemical composition of the environment that occur at the metal–dielectric interface can be monitored by the SPR measurement. This allows the detection of any pair of molecules that exhibits specific binding, which could be an antigen and antibody, a DNA probe and complementary DNA strand, or an enzyme and its substrate [\[5–13\].](#page--1-0)

The SPW arises from the energy transfer from the incident light wave (quantified as photon) into an electron charge density wave or SPW (quantified as plasmon) at the surface of a solid which has a free electron-like structure. When the energy of the light is coupled into the metal's surface, collective resonance of electrons can be

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generated. The energy transfer from photon to plasmon is regarded as surface plasmon resonance (SPR) [\[14,15\].](#page--1-0)

The most widely used method to excite SPR is known as Kretschmann prism-coupler-based SPR, in which the incident light passes through an optically dense medium, usually a prism, to match the wave vector of the SPW. The metal film is deposited directly onto the prism surface [\[16\].](#page--1-0) The surface plasmons are excited at the metal/air interface. Since the surface plasmon is transverse magnetic (TM), SPR has to be excited by a light beam with p -polarization (TM mode). The resonant condition is tuned by either varying the angle of the incident light at fixed wavelength or varying the wavelength of the incident light at fixed incident angle; these are referred to as angular modulation and wavelength modulation, respectively [\[14\].](#page--1-0) When the resonant condition is satisfied, a sharp decrease in reflectivity occurs where the energy of incident light is almost completely absorbed and transferred from photon to plasmon. The resulting dip in reflectance *vs. light inci*dent angle θ is often referred to as the SPR curve.

The SPR curve is usually characterized by three major features: the resonant angle θ_R , the minimum reflectance or resonant depth R_{min} and the width of the resonant curve $\Delta\theta$ [\[17,18\].](#page--1-0) In biosensor applications of the prism-couplerbased SPR, the analyte under test is placed on the metal interface performing as the second medium of the prism/ metal/analyte configuration. Any changes in refractive index or thickness of the analyte result in changes of the wave vector of the SPW, hence the changes of the resonance curve features. From these changes, the changes of the analyte can be elicited. All the features of the SPR curve are dependent on the incident wavelength, dielectric constant and thickness of metal film, and the refractive index of the prism as well as the analyte [\[14\]](#page--1-0). There are many ways to modulate the resonant condition by various combinations of the above factors in a SPR configuration. To achieve better performances of the SPR sensor, optimized combinations of SPR configuration should be developed from case to case.

The technology of SPR biosensors based on the conventional Kretschmann configuration has been well developed. All kinds of means to improve its performances have been widely studied. The achievements of all these studies have been adapted and integrated into commercialized SPR systems. It has been said that there is not much room for further improvement in traditional SPR sensors. Therefore other development strategies and new approaches have to be explored.

One recent effort is the application of the multiple-phase Kretschmann configuration, in which an intermediate dielectric layer is intercalated between the prism and the metal film, as shown in Fig. 1. It has been confirmed that the introduction of an intermediate dielectric layer results in much larger propagation lengths of SPW along and perpendicular to the interface because the electric field of SPW is significantly redistributed across the multilayer structure, with a large fraction of the electric field existing in the less

Fig. 1. Schematic of multilayer SPR.

low loss intermediate dielectric layer; while for its counterpart, the conventional SPW decays rapidly within the high loss metal. Consequently, the multilayer SPR would exhibit a sharper resonance curve with a narrower resonance width in comparison with the conventional SPR [\[19,20\].](#page--1-0)

In general, in any measuring system utilizing the resonance phenomenon, a sharper resonance behavior means a greater sensitivity and a better resolution of the measurement. In the case of SPR biosensing, a sharper SPR curve (a narrower band width) would definitely result in greater sensitivity and finer resolution. The exact relation between the two factors is rather complicated. The sensitivity of a SPR biosensing system is a colligated parameter relating to many aspects of the measurements, such as the characteristics of the system (resolution, noise level, etc.), the measuring mode (measurants, fixed or variable angular mode, fixed or variable wavelength mode, etc.), and physical and biological aspects of the analyte samples (gaseous or liquids, film or bulk, etc.). It should be ideally investigated from case to case, but here we used the width of the resonance curve as a criterion to compare various SPR configurations.

The widths of the SPR curves, as discussed above, are affected by many factors. The dielectric constant and thickness of the metal film have very strong effects on the features of the resonant curve. It is widely recognized that silver (Ag) results in the sharpest resonance curve [\[21\].](#page--1-0) The wavelength of the incident light also has a strong effect on the resonant characteristics. A longer wavelength results in a lower resonant angle and a sharper resonant curve. Brink et al. [\[22\]](#page--1-0) suggested that working in the near-infrared range would result in greater sensitivity.

The refractive index of the prism also affects the resonant behavior. Our experimental results and computer simulation revealed that a higher refractive index of the prism results in a lower resonance angle and a sharper resonant curve. To obtain a high-performance SPR biosensor, the above three factors should all be taken into account. Ideally, an SPR set-up using a prism with high refractive index coated with a reasonable thickness of silver working under a near-infrared wavelength would deliver the sharpest resonant curve and highest performance. However, there are many practical restrictions. For example, most SPR systems use gold film instead of silver because of the high chemical inertia and very good bioaffinity of the gold film.

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