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A silicon-black phosphorous based surface plasmon resonance sensor for the detection of NO₂ gas

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ABSTRACT

In the presented article a silicon- black phosphorous based surface plasmon resonance sensor is proposed for the detection of NO_2 gas. This sensor takes the advantage of specific attachment property of NO_2 gas at the surface of black phosphorous nanolayer. The high purely real refractive index of silicon is utilized for the enhancement of sensitivity by a large factor. The performance defining parameters like shift in resonance angle, minimum reflectance, beam width of reflectance curve, and penetration depth are calculated and compared also.

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1. Introduction

Optical sensors are the fastest sensing technique for the detection of gas, chemicals, and biomolecules. Depending on their working principles, the optical refractive index (RI) sensors could be roughly divided in three vast categories: ray optics, wave optics (far field optics; field is far greater than wavelength), and nano optics (near field optics; field is approximately equal to wavelength). The ray optics based RI sensors are rely on refraction and reflection e.g. Abbe refractometers [1] and Differential refractometer [2]. These sensors are complicated to achieve higher spatial resolution for higher sensitivity. The wave optics based RI sensors rely on diffraction [3], forward/backward scattering [4], and various interference effects e.g. Fabry-Perot [5], Mach-Zehnder [6], Michelson [7], low coherence [8], fibre Bragg grating [9], and long period grating [10]. The far field optics based sensors has limited sensitivity. In contrast to ray optics and wave optics, nano optics based sensors are more attractive which utilize the evanescent waves in the subwavelength region near the interface of two media. The remarkable near-field optics based RI sensors are: whispering gallery modes (WGM) of micro-resonators [11]. slab waveguide [12], optical tunnelling effect [13], photonic crystal fibres (PCF) [14], and surface plasmon resonance (SPR) [15]. For WGM RI sensors, the Q factors of micro-resonators requires more strict processing precision and thermal stability. Loading and unloading of samples are inconvenient. The slab waveguides suffers from the coupling of light and needs great effort due to which these type of sensors are limited for commercialization. The PCF and SPR sensor have complementary sensitivity in terms of shift in resonance angle and penetration depth. The shift in resonance angle of SPR is higher than the PCF whereas the penetration depth of PCF is higher than the SPR. PCF sensors can detect small (<300 nm) as well as large (even upto 2500 nm) molecules because of its high penetration depth. But, for the detection of lower dimension molecules

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Short note







Fig. 1. Kretschmann configuration based four different SPR sensor structures in which light is coupled through prism.

PCF is not suited well because of its lower shift in resonance angle. Moreover, the fabrication of PCF chip is much difficult than SPR. In contrast, SPR is much suitable for the detection of lower dimension molecules because its penetration depth is sufficient for the detection in addition with the large shift in resonance angle and ease of fabrication. Thus, SPR based sensors could be best suited for the detection of nitrogen dioxide (NO_2) gas.

Naturally, NO₂ generates from the forest fires and atmospheric lightning discharges. The major anthropogenic sources of NO₂ are motor-vehicle exhaust and emissions from the commercial and industrial combustion processes. NO₂ is widely used as a nitrating agent in explosives, intermediate in nitric acid production, a polymerization inhibitor for acrylates, an oxidizing agent in rocket fuels, a bleaching of flour etc. NO₂ is a toxic gas and hazardous to health. The inhalation of NO₂ bothers dyspnea, mucos membranes, and inciting cough. The lung functioning and pulmonary tract are highly affected by inhalation of higher concentration of NO₂. The detailed study of toxic effects of NO₂ gas on human and animals are presented by national research council, Washington D.C. [16]. The NO₂ can be recognized if the odour threshold of it in air is 0.1–0.4 ppm [17]. Hence, once again SPR is best suited for the detection of such a lower concentration of NO₂.

The NO₂ in dry air can be detected by getting absorbed on the black phosphorous (BP) nanosheet at room temperature. BP is the most stable allotrope of phosphorous. BP nanolayers are stacked through van der Waals interactions. The exposure of NO₂ gas on the BP nanosheet increases the electrical conductivity. NO₂ withdraws electrons from the BP after getting absorbed on the BP surface because NO₂ is an oxidizing agent. Increase in electrical conductivity increases the extinction coefficient of BP. BP did not absorb the other gases e.g. CO, H₂S, H₂ etc. even at very high concentration [18]. Thus, the BP is capable of highly selective or specific detection of the NO₂ gas in the presence of CO, H₂S, and H₂.

The sensitivity of the SPR sensor increases with the real part of the RI of the add layer above the surface plasmon (SP) active metal layer [19]. Silicon (Si) can enhance the sensitivity of the SPR sensor by increasing the shift in resonance angle just because of its high purely real refractive index (RI) i.e. 3.916 at 632.8 nm operating wavelength [20]. Thus, Si can be introduced between the SP active metal layer and BP nanolayer to enhance the sensitivity in order to detect the NO₂ gas.

2. Design consideration and principle of operation

A schematic of Kretschmann configuration based SPR sensor in which light is coupled through prism is drawn in Fig. 1. In the Kretschmann configuration based SPR senor a thin surface plasmon active metal layer (Silver) is deposited on prism (SF11) [15]. In Fig. 1, four structures are shown depending on dielectric layers between sensing medium (SM) and SP active metal layer; Structure-I (SF11/Ag/SM), Structure-II (SF11/Ag/Si/SM), Structure-III (SF11/Ag/BP/SM), Structure-IV (SF11/Ag/Si/BP). The sensing medium is comprised of mixture of gasses e.g. NO₂, CO, H₂S, and H₂ in dry air. The sensing medium is created in a cuvette which is facilitated with inlet and outlet valve to pass in and pass out of the mixture of gasses. The RI, at 632.8 nm wavelength, of SF11 prism (n_p), silver (n_{ag}), silicon (n_{si}), five layered BP (n_{bp}), and SM (dry air, n_{sm}) are 1.7786 [21], 0.051255+4.3165*i* [22], 3.916 [20], 3.5+0.01*i* [23], and 1 respectively, and the thicknesses are semi-infinite, 52 nm, 5 nm, semi-infinite respectively. As the gasses are mixed in the dry air its RI changes above 1. Since only the NO₂ gas is absorbed on the surface of BP, concentration of NO₂ gas is responsible for increasing the RI of dry air near the surface of BP say 1–1.1.

A p-polarized light wave of 632.8 nm wavelength, generated from He-Ne laser source, is focused on one of the lateral plane of the prism. This prism couples the light to the deposited SP metal film. With the effect of attenuated total reflection (ATR), the evanescent field of coupled light excites the plasmon wave at metal surface which propagates along the interface of metal-dielectric. The wave vector of this surface plasmon wave (SPW) can be changed by varying the incidence angle (θ)

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