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RESEARCH ARTICLE

# SPR sensor for detection of heavy metal ions: Manipulating the EM waves polarization modes

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**Abstract**

The development of high sensitivity surface plasmon resonance (SPR) sensor depends on few crucial factors such as types and thicknesses of metal thin films, light coupling techniques and suitable polarization modes of EM waves. This work was carried out to investigate the effect of EM wave polarization modes on the sensing properties of SPR sensor in detecting heavy metal ions namely mercury (Hg) and plumbum (Pb). Three types of light polarization modes such as p-polarized, s-polarized and circular-polarized light were introduced. Gold and silver thin films with thicknesses of 50nm were deposited on top of SPR layer system to excite surface plasmon polaritons (SPPs). The SPR curves were analyzed by studying the FWHM, Q-factor and angle shifting characteristics. We managed to prove theoretically that the SPR phenomena able to be created by using not only the p-polarized light, yet by employing a circular-polarized light. The sensor showed positive respond for both polarization modes, where the troughs were red-shifted about 23.78% as Pb was introduced on the top of the gold-coated SPR sensor. The SPR angles were shifted about 24.45% as the sensor was exposed with Hg metal ions. Different response due to the presence of different analytes exhibited excellent criteria of high selectivity sensor. In conclusion, the combination of p-polarized light or circular-polarized light and gold thin film able to accentuate the significant role of SPR sensor in detecting heavy metal ions.

***Keywords***: SPR sensor, EM waves polarization modes, heavy metal ions, optical sensor



## INTRODUCTION

Water pollution is contamination of water by foreign matter that reduce the quality of water. Most of the pollutants such as lead (Pb), arsenic (As) and mercury (Hg) are very harmful (Verma *et al*., 2013) Water contamination by heavy metals is a common issue encountered in many countries due to industrial and urban wastes in water resources which give health and socio-economic impacts (Borah *et al*., 2014). There are several methods have been introduced to detect the presence of heavy ions metals such as enzyme sensor, electrochemical sensor, piezoelectric sensor etc (Bagal *et al*., 2008; Cui *et al.*, 2008; Ghica *et al*., 2008; Huang *et al*., 2007). However, there are few weaknesses of these methods such as sophisticated procedure and costly. The development of suitable sensors with high responsivity, excellent sensitivity and and less expensive are increasingly becoming a priority.

Today, the developments of optical sensors are growth rapidly. The demand of fiber optics sensors (Verma *et al*., 2015; Zhao *et al*., 2013) and free space optics sensors (Li *et al*,. 2014; Nizamiv *et al*., 2015) indicate the society's acceptance to these technologies. Nonetheless, the applications for each sensor are limited to certain applications such as for gas sensing (Viter *et al*., 2015), liquid sensing (Wang *et al*., 2014), chemical sensing (Askim *et al*., 2013) etc. In recent years, Surface Plasmon Resonance (SPR) is one of the common technique for sensing purpose. SPR phenomena involving the interaction of matter and light. It occurs when the polarized light which is under total internal reflection (TIR) conditions strikes the metal thin film layer with dielectric negative that has been placed at the interfaces between two dielectric media of different refractive angle through the prism (Mukhtar *et al*., 2013).

SPR sensor is one of the favourable optical sensors due to its high sensitivity (Murat *et al*., 2016; ). Many works have been conducted to optimize the SPR signals by controlling the metal's thicknesses, introducing semiconductor materials and depositing metal nanoparticles. Critical factors that need to be addressed is to ascertain the stability and the accuracy of SPR sensor system itself. Based on previous studies (Mukhtar *et al*., 2014; Liu *et al*., 2016), light polarization mode is one of the main criteria that need to be obeyed to generate SPR. The main objective of this work is to study the effect of EM wave polarization modes on the sensing properties of SPR sensor in detecting heavy metal ions. By fixing the control parameters such as properties of metal thin films, light polarization modes and dielectric constants of analytes; the characteristics of SPR curves were investigated.

## EXPERIMENTAL

### Methods

A red laser with excitation wavelength of 633nm was employed as a light source. Types of polarization modes were varied as p-polarized, s-polarized and circular-polarized. The existence of Brewster angle and location of critical angle were investigated by observing the behavior of reflected light from a bare prism. The appearance of Brewster angle is an important indicator for the excitation of surface plasmon polaritons (SPPs) (Mukhtar *et al*., 2013a). The values of incident angles were modulated from 38° to 70°. For excitation of SPR signals, two types of metal thin films namely silver (dielectric constant, $\varepsilon_s$= -17+0.7i) and gold (dielectric constant $\varepsilon_g$= -9.39+1.09i) with thicknesses of 50nm were appointed. By tuning the angle of light incidence of the totally reflected beam inside the prism, the resonance condition for excitation of SPPs can be fulfilled (Novotny *et al*., 2006). Figure 1 displays an example of SPR experimental setup for detection of the targeted analytes (Mukhtar *et al*., 2013b). To observe the significant role of SPR sensor in detecting the heavy metal ions, plumbum (Pb) and mercury (Hg) with values of dielectric constant $\varepsilon_{Pb}$=3.5344 and $\varepsilon_{Hg}$=3.9026 respectively, were introduced on top of metal thin films. Table 1 tabulates the values and properties of four-layer system of SPR sensor. The important parameters such as Q-factor, full width half maximum (FWHM) and angle shifting were analyzed.

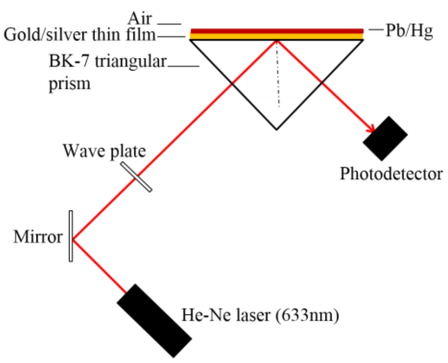


**Fig. 1** Illustration of SPR experimental setup for heavy metal ions (Pb/Hg) detection. The function of optical waveplate is to modulate the polarization mode of EM waves.

**Table 1** The four-layer system of SPR sensor.

| Layer | | Types | Thickness, *t* (nm) | Value of dielectric constant, ε | |
|---|---|---|---|---|---|
| | | | | Real part | Imaginary part |
| 1 | Prism | dielectric | none | 2.29 | 0 |
| 2 | Metal | gold | 50 | -9.39 | 1.09 |
| | | silver | 50 | -17 | 0.7 |
| 3 | Heavy metal ions | Plumbum (Pb) | none | 3.5344 | 0 |
| | | Mercury (Hg) | none | 3.9026 | 0 |
| 4 | Air | dielectric | none | 1 | 0 |

## RESULTS AND DISCUSSION

Figure 2(a) depicts the location of critical angle as light polarization modes were set as p-polarized, s-polarized and circular polarized. It was found that the critical angles situated at 39.5° only existed for p-polarized and circular polarized modes, in which the total internal reflection (TIR) phenomena were occurred. It is important to monitor the position of critical angle because this value can be used as the location's indicator of SPR angle. The location of SPR angle is always within the range of TIR (Novotny *et al.*, 2006). In this work, the location of SPR angles were expected to be above 39.5°. Below this angle, SPR cannot occur due to the insufficient energy provided by the incident light (Novotny *et al.*, 2006). About 91.93% of the incident light experienced TIR as it was set under p-polarization mode. As the mode was changed into circularly-polarized, 60% of incident light was totally reflected. Those percentage amounts of reflected light will be consumed to generate SPPs. Obviously, the TIR phenomena cannot be established as the polarization mode was designated as s-polarized. The presence of Brewster angle (circle-dashed line) also can be used as an indicator for the existence of SPR phenomena (Mukhtar *et al.*, 2013a). It was found that only p-polarized and circular polarized light indicated the appearances of Brewster angles at 27.5° as captured in Figure 2(b).

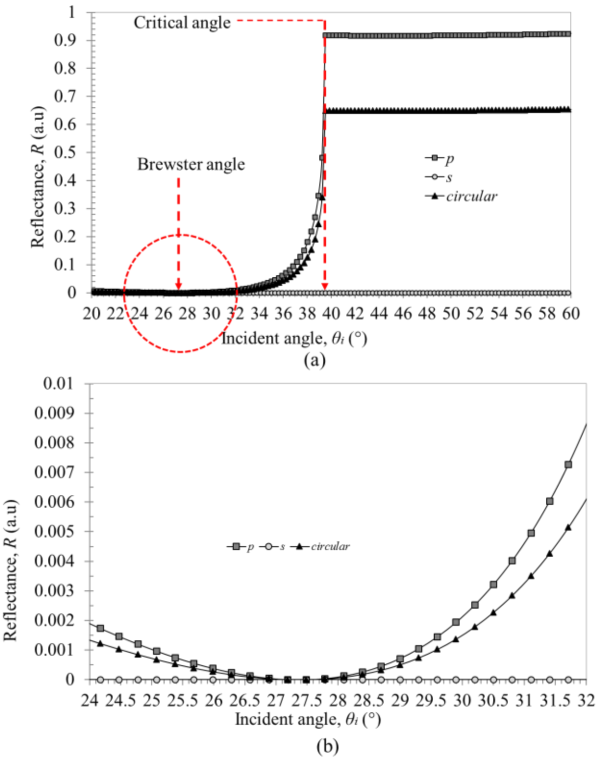


**Fig. 2** (a) Location of critical angle and Brewster angle using triangular prism with refractive index of 1.51 for various light polarization, (b) Zoom-in the location of Brewster angle from Figure 2(a).

Figure 3 displays the SPR curves as gold thin films were coated on the glass substrate. Minimum values of R=0 for three types of polarization modes were obtained. Note that the justification of strong SPR signals were not genuinely represented by the value of minimum reflectance; to be exact, the SPR curve depth or Q-factor analyses able to explain this properties. Obviously, s-polarization mode resulted the absence of SPR signal which indicates an excellent agreement with Figure 2. This result clarified the crucial role of Brewster angle in determining an appropriate polarization mode for the establishment of SPR. In comparison between circular and p-polarized modes of incident light with the usage of gold thin film to excite SPPs, (Figure 3(a)), the circular polarization mode resulted weaker SPR signal than p-polarized where only 60.23% of the incident light were excited as SPPs, meanwhile about 85.33% of the incident light were generated as SPPs for p-polarized light. The FWHM value of 2.931° for p-polarization mode was smaller than the circular mode. For circular polarized light, the FWHM was obtained as 3.1034°.

As type of thin film was replaced with silver, the values of FWHM were drastically reduced by observing the decrease of SPR curves' width. The values of FWHM of p-polarized and circular polarized modes were nearly the same which are $FWHM_{p\text{-}polarized}$=0.25° and $FWHM_{circular\ polarized}$=0.23°. As expected, same characteristics of light reflectance behaviour were observed where no SPR signal was produced as s-polarized light was appointed. Strong signals about 89.60% was resulted with the employment of p-polarized light and 63.35% for circular polarized light. According to these results, it can be summarized that SPPs can be excited by manipulating the light polarization modes either into p-polarized or circular polarized. s-polarized mode happens to result no SPR signal by considering the characteristics of EM waves where the oscillation of electrons are on the same direction with the glass plate, meanwhile for p-polarized light the SPPs were perpendicularly oscillated on the glass surface where the SPR signals can easily be observed (Saleh *et al*., 1991).

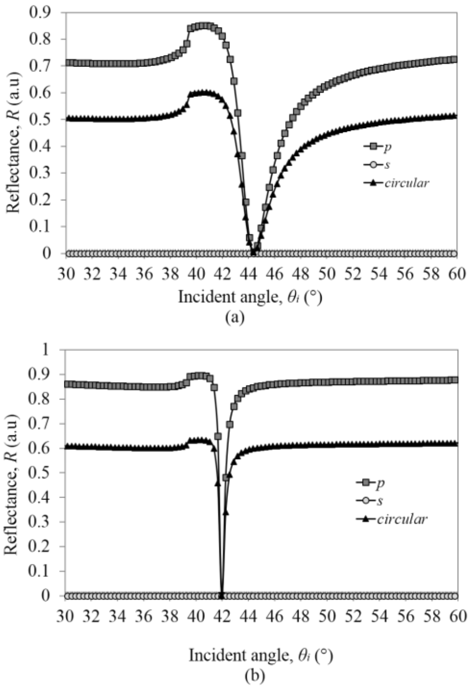


**Fig. 3** SPR curves for several types of polarization modes namely p-polarized, s-polarized and circular polarized by using (a) gold thin film (b) silver thin film.

To study the role of light polarization modes on the sensitivity of SPR sensor, two types of analytes were introduced on top of metal thin film, namely mercury (Hg) and plumbum (Pb). Figure 4(a) displays the characteristics of SPR signals with the employment of gold thin film. The sensor showed positive respond for both polarization modes, where the curves were red-shifted about 23.78% from 44.37° to 54.92° as Pb was introduced on the top of the sensor. For p-polarization mode, the FWHM value was increased about 73% to 10.855° when the SPR sensor reacted with Pb. As the polarization mode was changed into circular mode, the FWHM was obtained as 10.560° with 70.61% of increment in comparison with the absence of analyte. The influence of metal thin film's types on the sensor sensitivity was investigated by replacing gold thin film with silver as captured in Figure 4(b). The SPR angle was shifted about 12.22% from 41.96° to 47.09°. The observation of angle shifting exhibits the ability of SPR sensor to detect the presence of Pb metal ions. This output shows that gold results better sensitivity than silver due to its strong response. The properties of silver which are reactive and easily oxidized contribute to the less sensivity performance of SPR sensor (Akowuah *et al.*, 2012).

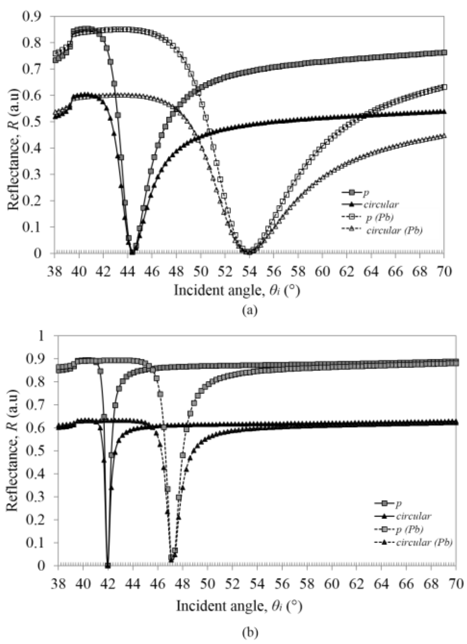


**Fig. 4** SPR signal responds with the presence of Pb ions (a) gold thin film (b) silver thin film.

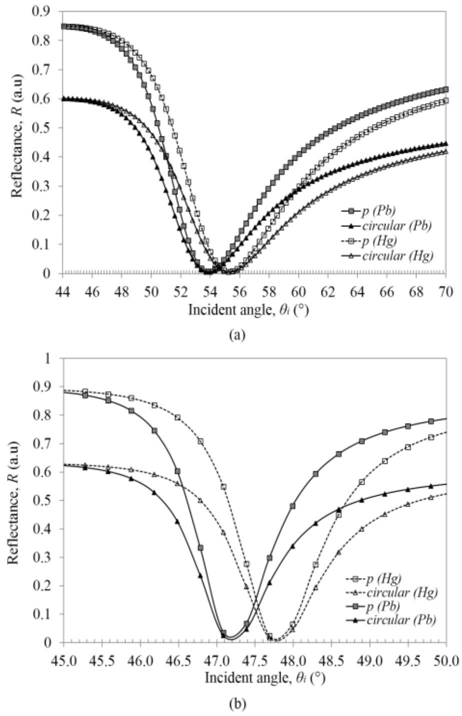


**Fig. 5** SPR signal responds for the detections of Hg and Pb metal ions with employments of (a) gold thin film (b) silver thin film.

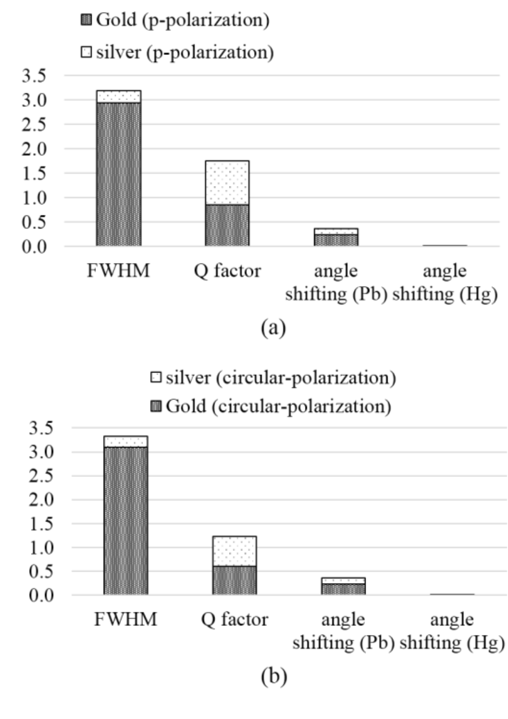


**Fig. 6** Parameter analyses on the performance sensitivity of SPR sensor using (a) p-polarized light (b) circular polarized light.

One of the important features of an excellent potential optical sensor is its ability to differentiate various types of analytes or can be simplified as selectivity. To achieve this, we compare the SPR signal response as Hg and Pb metal ions were introduced on top of the sensor. Figure 5(a) shows the angle shifting experienced by SPR sensor embedded with gold thin film as different analytes were added on top of the sensor. As Pb was replaced with Hg, the SPR angles were shifted about 0.5% from 54.92° to 55.22°. However, types of polarization mode, neither p-polarized nor circularly polarized did not result any impact on SPR angle shifting where both modes experienced same amount of shifting. By substituting Hg metal ions, the SPR curves experienced 1.27% of shifting for silver thin film as depicted in Figure 5(b).

Figure 6 summarized the analyses parameters on the sensitivity performance of SPR sensor. The analysis of FWHM between p-polarized and circular-polarized portrayed similar behaviour where large FWHM was obtained by employing gold thin film. Q-factor analysis indicated that the usage of p-polarized light with the assistance of gold thin film for SPPs generation produced deeper SPR curve depth than circular-polarized which explains the cability of these combinations to yield strong SPR phenomena. In comparison with silver, the development of high sensitivity SPR sensors can be achieved by employing 50nm gold thin film where apparent angle shifting was observed as heavy metal ions were introduced on the sensors. The ability in detecting different types of analytes namely Pb and Hg based on amount of angle shifting indicates an impressive selectivity features of gold-coated SPR sensor.

## CONCLUSION

This study investigates few crucial parameters which affect the performance of SPR sensors by controlling type of light polarization modes. It was found that the Q-factor values which represents by the SPR curve depth plays a significant role in achieving excellent SPR sensor. The major finding of this work proves that the SPR phenomena able to be created with the usage of circular-polarized light, apart from p-polarized light. In conclusion, the combination of EM wave p-polarization mode and gold thin film able to accentuate the significant role of SPR sensor in detecting heavy metal ions.

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