Bimetallic Ag/Au thin films in Kretschmann-based surface plasmon resonance sensor for glucose detection

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The surface plasmon resonance (SPR)-based sensor performance was investigated in bimetallic silver/gold (Ag/Au) thin films. This study aims to examine SPR-sensing performance of the various thickness of Ag/Au to obtain the optimum sensitivity and figure-of-merit (FOM) for glucose detection, compared to Au thin films. Finite-Difference-Time-Domain (FDTD) simulation was used to evaluate the Kretschmann configuration in angular interrogation at 633nm wavelength. Bimetallic Ag (30 nm)/ Au (17.5 nm) thin-film gave better sensing performance since the transfer of silver (Ag) electrons to Au increased the density of surface plasmons in the bimetallic structure, shown by FOM and sensitivity value as 0.5173 and 4.7993°/RIU, respectively.

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1. Introduction

Studies on glucose sensors present a growing field, especially in the medical technology field. The limitations of finger-stick blood testing as the most-commonly used glucose monitoring platform has increased the research towards the development of non-invasive glucose sensors [1,2]. Label-free and real-time features serve as a fundamental property in order to improve performance and reduce operating costs of sensors [3]. Surface Plasmon Resonance (SPR)-based sensors that provide these features become a growing research topic in the last decade.

SPR-based sensor is one of the optical sensors that utilizes surface plasmon wave (SPW) phenomenon. SPW is p-polarized electromagnetic waves that propagate at the metal-dielectric interface [4] and can be excited by the specific resonance condition dependent on the angle, wavelength and intensity of the incident optical wave [5]. Detection activity occur when the resonance conditions are varied by a change of background dielectric constant or refractive index of analytes on the uppermost metal surface [6].

SPR-based sensors are applied for various biochemical detection; therefore, the metals used in the configuration must have high mechanical and chemical stability, also good conductivity and transparency [7]. Due to their characteristics, noble metals such as Au, Ag or Cu were chosen for this purpose [8]. Among the noble metals, Ag has better propagation length, penetration depth and field concentration for its SPW characteristics [9]. However, Ag has a lower chemical stability.

Therefore, the lowest reflectivity in the SPR curve can be provided by the silver thin film which has also been reported to give enhanced sensitivity to refractive index and thickness variation compared to gold thin films [10,11]. The SPR-based sensors using gold thin film was executed in a previous study and proved its high performance in the detection of glucose [12]. In order to get the benefits from both noble metals, many studies have investigated the most efficient technique in combining gold and silver (bimetallic technique). In prior work, core-shell nanoparticles were dominantly studied as a technique for Ag/Au bimetallic effect [13]. However, due to the ease of fabrication and utilization of the SPR, thin-film types are preferable than those of core-shell nanoparticles technique [14]. Although the bimetallic thin films of Ag/Au in SPR-based sensor have been studied previously, it is infrequent to find specific studies of its application in a glucose sensor [15]. A recent work by Miyazaki et al. showed a minimum detection of 10 µM of glucose with a resonant angle shift of 0.02° after a long duration of 20 minutes using Kretschmann-based SPR at 670 nm only but no values of glucose molarity RI were disclosed [16].

Nowadays, simulation is a must and useful step in research to gain optimum results prior to fabrication and experiments. In any research field, especially optical field, Finite Difference Time Domain (FDTD) solutions have a variety of geometric shapes consisting of various types of materials, including dielectric, magnetic, frequency-dependent, nonlinear, and anisotropic materials, like wide-angle broadband[17], tunable terahertz add-drop filter [18], and photonic crystal fiber [19]. The theoretical work of FDTD is generally to solve the complex Maxwell's equation [20]. FDTD approach provides a single run ability to calculate both the spatial and temporal properties [21-26]. Various commercial software has been developed based on the FDTD approach such as Lumerical, XFDTD, and SEMCAD [14].

This study aims to find the best parameter of bimetallic Ag/Au thin films in Kretschmann-based SPR sensor for glucose detection, by varying the film-thicknesses to sense various glucose concentrations. The glucose concentration is varied based on sugar level parameters in fasting blood sugar (FBS) test for diabetes diagnosis. A patient with a sugar level below 0.1 g/dL is stated normal and turn to pre-diabetes when exceeds that value. The dangerous sugar level is above 0.14 g/dL, which indicates diabetes [27]. Each variation has been evaluated using FDTD simulation. The sensor performance is exhibited by the sensitivity and signal-to-noise ratio (SNR) as a figure of merit (FOM), which is then compared to Au thin films which are the most commonly used materials in SPR-based sensor for glucose detection [8, 12].

2. Simulation design

In this study, FDTD solutions (Lumerical Inc.) is used to perform an angular interrogation of the surface plasmon resonance phenomenon in Kretschmann configuration, using 633 nm optical wavelength. Fig. 1(a) shows the simulated sensor design based on Kretschmann configuration in XY view; which consist of the sensor chip layer-by-layer (Fig. 1(b)), the sweep component of optical source is shown in blue and purple arrow while the front and back power monitor component is shown as a yellow line.

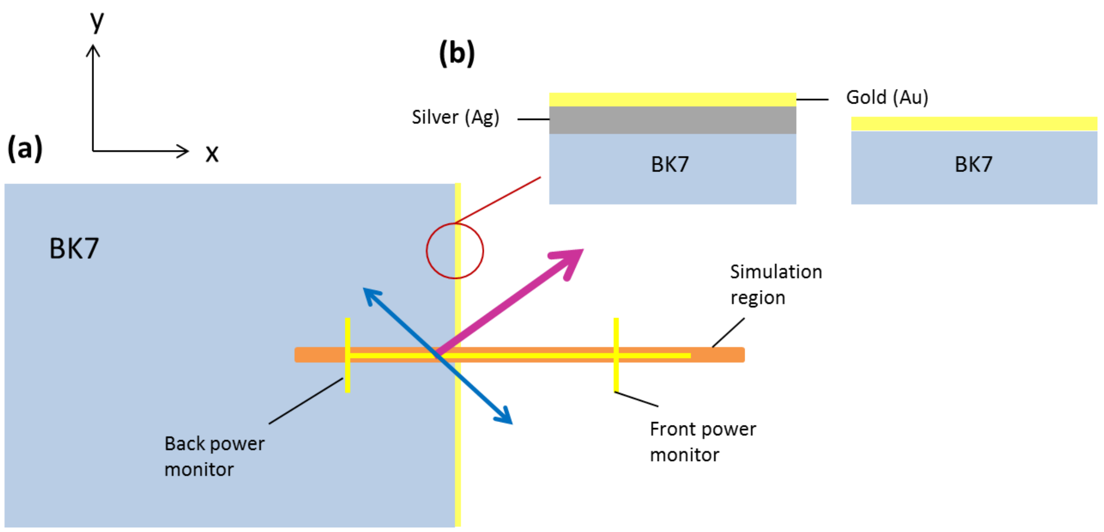


Fig. 1. (a) Simulation display in Lumerical FDTD; (b) Sensor chip configuration (color online)

The sensor chip consists of a substrate layer and the thin-film layers. BK7 glass substrate with thickness of 795nm and refractive index of 1.5210 was used as a prism/substrate layer, which forms the basis for the bimetallic thin film deposition. The bimetallic silver-gold (Ag/Au) thin films or single metal gold (Au) thin-film is above the substrate and stand as the sensing surface (n_{Ag} = 0.1567, k_{Ag} = 3.7987; n_{Au} = 0.1968, k_{Au} = 3.2478) (Fig. 1(b)). The SPR phenomenon is produced when the *y*-component of the source wave vector matches with the wave vector of the SPR mode in the bimetallic metal layers. Using numerical analysis, the parameters of the plane-wave source is directed to the metal layers in a sweep manner over a range of incident angles to obtain the resonance angle to excite the SPR mode, ranged in 35° to 55° in air, while 60° to 90° in glucose. This mode will be detected by the back-power monitor placed behind the source to measure the reflection of the structure [28].

Initially, FDTD simulation was performed to obtain the change in reflectivity versus incident angle in the SPR response curve, corresponding to the thicknesses of bimetallic thin-film Ag/Au, assuming that the thin films were in contact with the air (n = 1.0000). The Au thicknesses were varied with thicknesses of 2.5, 5, 7.5, 12.5, 17.5, 18 and 22.5 nm, while the Ag thickness was maintained at 30 nm.

Afterwards, the optimum design was simulated in various concentrations of glucose as the background analyte which is 0.08, 0.14, 0.20, 0.30, 0.40 g/dL. Each concentration gives a different refractive index calculated using linear fitting to reported experimental data [29], based on the linear relationship between n and λ ($n=a+b\lambda$). The SPR phenomenon was also evaluated on a single metal sensor chip with 50 nm-thickness of nano-laminated gold (Au) in glucose solution for comparison purposes.

Performance of the sensor was evaluated in terms of its sensitivity and figure of merit (FOM) measured from the SPR response curve. The sensitivity (*S*) is the ratio between the change in resonant angle ($\Delta\theta_{SPR}$) to the change in refractive index (Δn) as shown in Equation (1), expressed in degrees per refractive index unit (°/RIU). While the FOM is represented by the ratio between the change of resonant angle to the full-width at half-maximum (FWHM), as shown in Equation (2). The FOM, is used to compare the performance of SPR.

$$S = \frac{\Delta\theta_{SPR}}{\Delta n} = \frac{\theta_{SPR(glu)} - \theta_{SPR(water)}}{\Delta n_{glu} - \Delta n_{water}} \quad (1)$$

$$FOM = \frac{\Delta\theta_{SPR}}{FWHM} \times 100 \quad (2)$$

3. Result and discussion

In order to characterize the performance of bimetallic Ag/Au thin films with different Au thicknesses, the reflectivity is plotted against the incident angle as obtained from the numerical analysis of FDTD solutions as shown in Fig. 2.

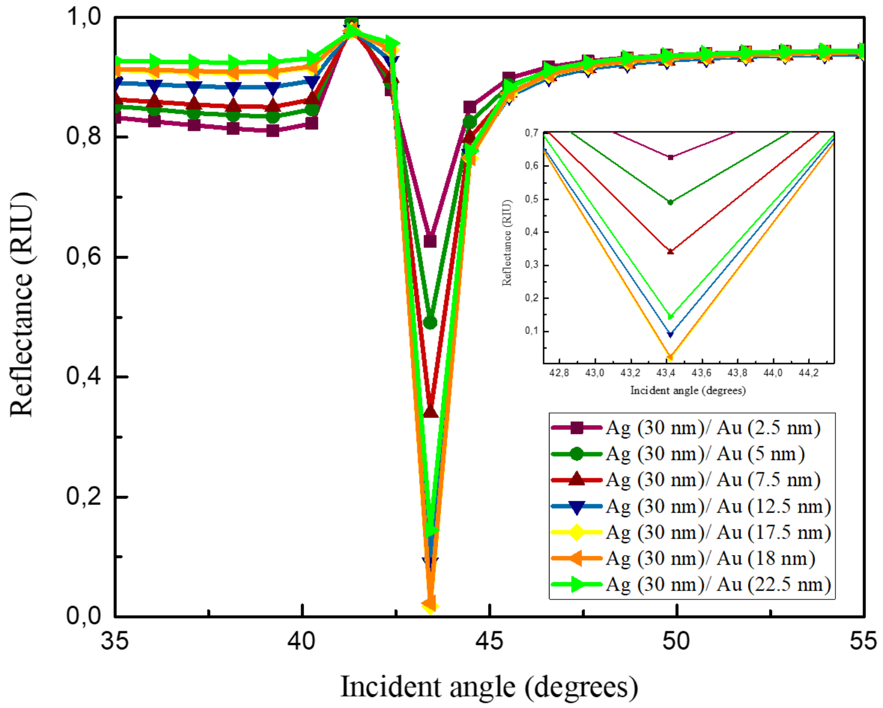


Fig. 2. SPR response curve for various thicknesses of bimetallic Ag/Au thin films in Kretschmann configuration of SPR-based sensor in air (color online)

Based on the principle of Attenuated Total Reflection (ATR), surface plasmon waves are excited when the incident wave experiences maximum energy loss, which results in minimum reflectivity. Thus, the point at which surface plasmon resonance occurs is shown by the dip in the SPR response curve [5]. As shown in Fig. 2, each variation has the same resonant angle (θ_{SPR}), which is 43.4210° respectively, but the minimum reflectivity is varied. The results indicate that Ag thickness of 30nm and Au thickness of 17.5 nm as the best thickness combination, since it shows the lowest dip of curve with R_{min} = 0.0176. Referring to previous studies, the smaller the value of minimum reflectivity, the better the sensor performance [30]. A smaller R_{min} value indicates a higher amount of energy transferred through thin films to oscillate the surface electrons, thereby strengthening the energy of the surface plasmon wave [5, 31].

Furthermore, to determine its performance in glucose detection, sensor chips with Ag (30 nm)/ Au (17.5 nm) was simulated in FDTD with changes in the background analyte to depict glucose solution refractive index. As shown in Fig. 3, the refractive index and concentration have a linear relationship, where increasing the concentration of the solution also increases the refractive index. Since the refractive index is obtained from a linear fitting, a perfect linear regression value of R^2 = 1 was obtained.

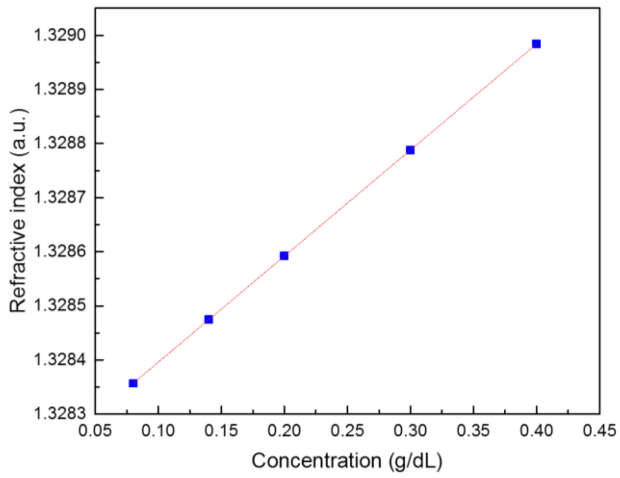


Fig. 3. Refractive index of different glucose concentration using linear fitting to experimental data

The incident wave is swept at the surface of the thin metal layer with incident angle ranging from 60° to 90°. Due to variations in the background refractive index, different resonant angles were obtained, shown by the SPR response curve shift. The shift width is proportional to the change in the refractive index [28], therefore a small change in the refractive index does not give a significant shift in the curve, as obtained in this study shown in Fig. 4 and Fig. 5.

Fig. 4 shows the SPR response curve from FDTD performed for Ag (30 nm)/ Au (17.5 nm) in various concentrations of glucose as the background analyte. The minimum reflectivity ranges between 0.0119 to 0.0120, while the resonant angle is in the range of 70.5747° to 70.6374°, with an average shift of 0.0156° from each other. The FWHM value averages 4.0508; it can be said that bimetallic Ag/Au layers have a narrow SPR spectrum.

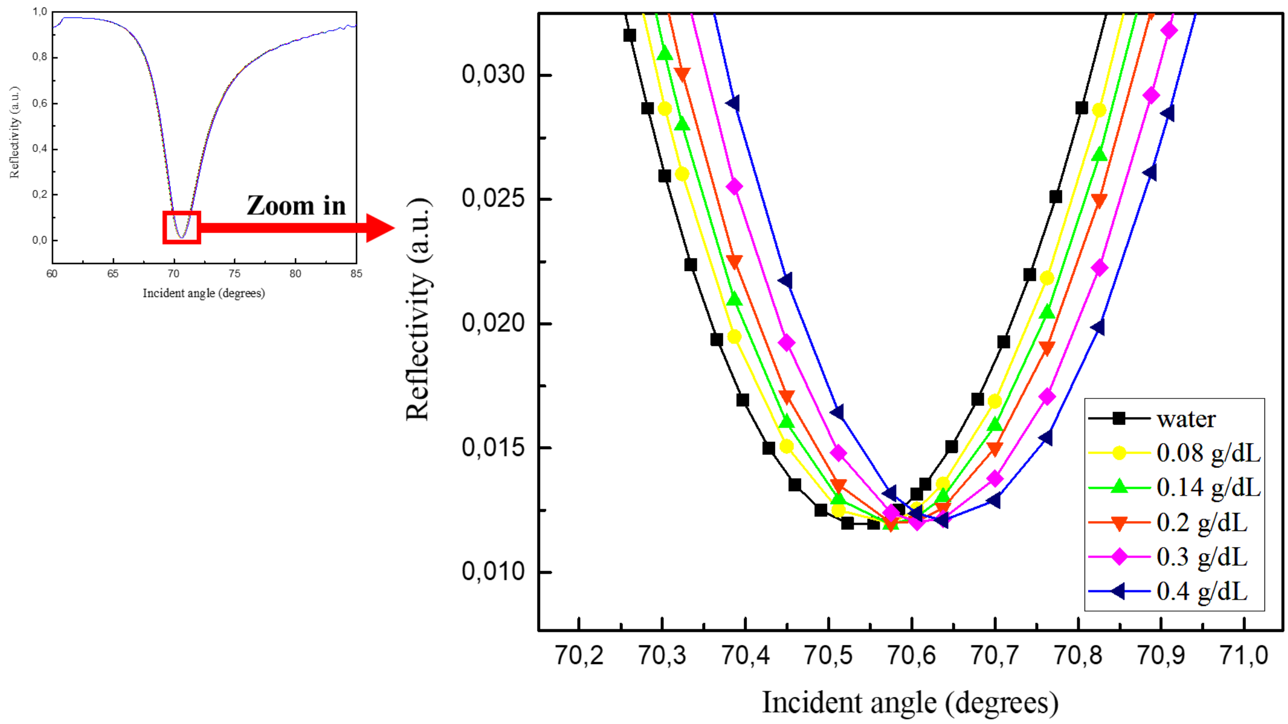


Fig. 4. The SPR response curve of Kretschmann configuration with bimetallic Ag (30 nm)\ Au (17.5nm) thin film for glucose detection (color online)

Similar results are indicated by the SPR response curve for Kretschmann configuration with a purely Au layer only with 50 nm thickness, as shown in Fig. 5. The resonant angle average shifted 0.0261° from each other in the range of 72.4242° to 72.5287°, with a minimum reflectivity ranging between 0.0090 to 0.0093. Compared to Ag/Au response curve, the Au response curve has a wider FWHM of 6.4575. FOM value is affected by FWHM, where the dependence is inversely proportional [14].

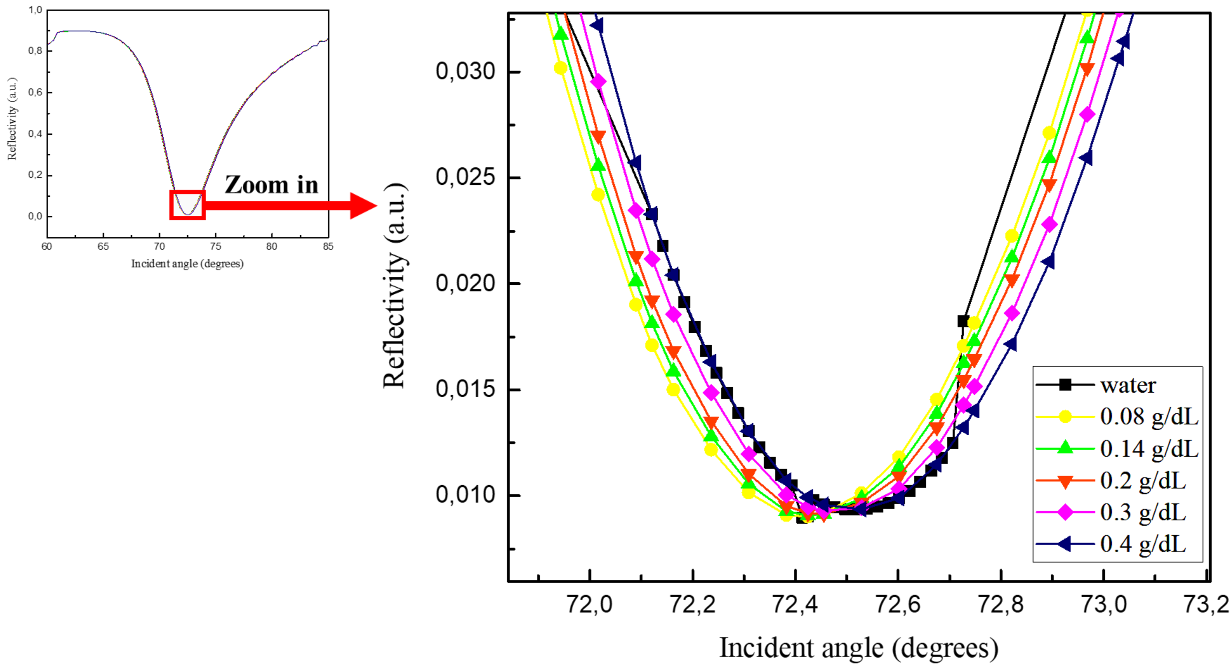
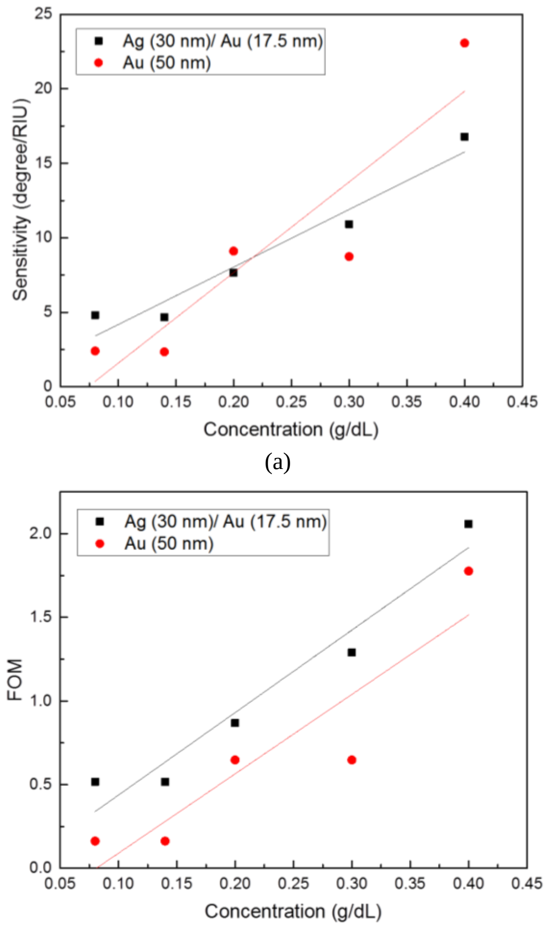


Fig. 5. The SPR response curve of Kretschmann configuration with Au (50nm) thin film for glucose detection (color online)

Further, the response curve for water sensing (n = 1.3240) was performed to be used as a baseline or reference to changes in the resonant angle, for both configurations. The curve provides resonant angle of bimetallic Ag (30 nm)/ Au (17.5 nm) in water as 70.5538°, and 72.4138° for single metal of Au (50 nm).

From the numerical analysis, the sensitivity and FOM has increased with the increment in glucose concentration. Due to the higher concentration, the change of refractive index on the metal surface becomes more significant. However, as shown in Fig. 6(a), the linear fitting between the sensitivity of bimetallic layers (R^2 = 0.9491) and single metal (R^2 = 0.8437) sensor chip crossed each other, there is no accurate comparison to show better performance. For example, in 0.08 g/dL glucose concentration, Ag (30nm)/Au (17.5nm) and Au (50nm) obtain 4.7993°/RIU and 2.3962°/RIU of sensitivity, respectively. While in higher glucose concentration of 0.4 g/dL, sensor chip with single metal obtained 23.0597°/RIU as a higher sensitivity compared to 16.7756°/RIU obtained by the bimetallic thin films. The sensitivity of bimetallic thin film is also worthy to be compared to another study of SPR-based sensor using gold thin film, which provide the glucose sensitivity of 3.64°/M or equal to 2.206°/RIU in the concentration of 4 mmol/L (1.61 g/dL) [12]. The presence of Ag thin film obviously enhances the performance of the bimetallic thin film SPR sensor in terms of its sensitivity.

Whereas, by evaluating FOM as displayed in Fig. 6(b), it is shown clearly that the sensor chip with Ag (30nm)/ Au (17.5 nm) gives better performance in the range of 0.5173 – 2.0574 (R^2 = 0.9474), which is quite significant compared to Au (50 nm) with FOM in the range of 0.1619 – 1.7761 (R^2 = 0.8439). Higher FOM is obtained due to a smaller FWHM in the SPR curve as well as a large change in the resonance angle.



(b)

Fig. 6. Performance comparison of Kretschmann-based SPR sensor between bimetallic and single metal thin film, shown in (a) Sensitivity; (b) Figure-of-merit (FOM) for different glucose concentration (color online)

Based on the results, the bimetallic Ag (30nm)/ Au (17.5 nm) thin-films are confirmed to have better performance than single metal Au (50 nm) thin-film, since it can be confirmed that the sensitivity is relatively improved when the FOM is large [14]. This is due to the higher conductivity values of Ag and Au layers versus a purely Au layer. This contributed to higher number of electrons interacting with the incident optical wave in order to produce a larger surface plasmon wave. On bimetallic Ag/Au thin film, the electron cloud oscillates in response to the positive charge of Au and suffers an attractive force from net positive charges of Au. Therefore, the bound grade has been decreased and the SPR peak shifts [14]. From the application perspective, this optical-based sensor design is promising to be applied in diabetes detection and monitoring technology because previously the range of detected blood sugar level is in the range of 0.1 – 0.14 g/dL [27], whereas this work has extended the range to lower limit of detection which is 0.08 – 0.4 g/dL.

4. Conclusion

This study set out to determine the combination of Ag/Au bimetallic thickness as a sensor chip of the surface plasmon resonance-based sensor with Kretschmann configuration. It observed that the Ag 30nm and Au 17.5nm gave the best performance compared to other Ag/Au thickness variations, shown by the lowest minimum reflectivity. In conclusion, we have confirmed that the Au/Ag bimetallic thin-film has better sensing performance than single Au thin-film for low glucose concentrations. For glucose concentration of 0.08 g/dl, the sensitivity and FOM was 4.7993°/RIU and 0.5173 respectively for bimettalic Ag/Au sensor chips at 633 nm optical wavelength.

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References

[1] P. Makaram, D. Owens, J. Aceros, Diagnostics **4**(2), 27 (2014).
[2] E. H. Yoo, S. Y. Lee, Sensors **10**(5), 4558 (2010).
[3] H. N. Daghestani, B. W. Day, Sensors **10**(11), 9630 (2010).
[4] J. M. Pitarke, V. M Silkin, E. V. Chulkov, P. M. Echenique, Rep. Prog. Phys. **70**(1), 1 (2006).
[5] C. M. Miyazaki, F. M. Shimizu, M. Ferreira, "Surface plasmon resonance (SPR) for sensors and biosensors. In Nanocharacterization Techniques", William Andrew Publishing 183-200 (2017).
[6] K. Kurihara, K. Suzuki, Anal. Chem. **74**(3), 696 (2002).
[7] B. F. Matarèse, P. L. Feyen, A. Falco, F. Benfenati, P. Lugli, J. C. deMello, Sci. Rep-UK **8**(1), 5560 (2018).
[8] M. Todeschini, D. S. F. A. Bastos, F. Jensen, J. B. Wagner, A. Han, ACS Appl. Mater. Inter. **9**(42) 37374 (2017).
[9] M. A. Ordal, L. L. Long, R. J. Bell, S. E. Bell, R. R. Bell, "Optical Properties of the Metals Al, Co, Cu, Au, Fe, Pb, Ni, Pd, Pt, Ag, Ti and W in the Infrared and Far Infrared" Missouri Univ-Rolla (1985).
[10] X. C. Yuan, B. H. Ong, Y. G. Tan, D. W. Zhang, R. Irawan, S. C. Tjin, Journal of Optics A: Pure and Applied Optics **8**(11), 959 (2006).
[11] S. Chah, E. Hutter, D. Roy, J. H. Fendler, J. Yi, Chemical Physics **272**(1), 127 (2001).
[12] P. S. Menon, B. Mulyanti, N. A. Jamil, C. Wulandari, H. S. Nugroho, G. S. Mei, N. F. Z. Abidin, L. Hasanah, R. E. Pawinanto, D. D. Berhanuddin, Sains Malays. **48**(6), 1259 (2019).
[13] O. Peña-Rodríguez, U. Pal, Nanoscale Res. Lett., **6**(1), 279 (2011).
[14] S. H. Kim, T. U. Kim, H. Y. Jung, H. C. Ki, D. G. Kim, B. T. Lee, J. Nanosci. Nanotechno. **18**(3), 1777 (2018).
[15] R. Kashyap, S. Chakraborty, S. Zeng, S. Swarnakar, S. Kaur, R. Doley, B. Mondal Plasmonics **6**(108), 1 (2019).
[16] C. M. Miyazaki, F. M. Shimizu, J. R. Mejía-Salazar, O. N. Oliveira Jr, M. Ferreira, Nanotech. **28**(14), 145501 (2017).
[17] B. Wu, J. Wang, Optoelecton. Adv. Mat. **12**(7-8), 417 (2018).
[18] L. J. Sheng, Y. J. Pei, Z. Le, H. J. Rong, Q. G. Hua, Optoelecton. Adv. Mat. **12**(3-4), 140 (2018).
[19] A. Bhatnagar, N. Singh, Optoelectron. Adv. Mat. **10**(11-12), 840 (2016).
[20] K. Yee, IEEE T. Antenn. Propag. **14**(3), 302 (1966).
[21] G. S. Mei, N. R. B Mohamad, N. A. Jamil, B. Y. Majlis, P. S. Menon, Sains Malays. **47**(10), 2565 (2018).
[22] N. A. Jamil, P. S. Menon, G. S. Mei, B. Y. Majlis, Sains Malays. **47**(5), 1033 (2018).
[23] P. S. Menon, F. A. Said, G. S. Mei, M. A. Mohamed, A. R. M. Zain, S. Shaari, B. Y. Majlis, Sains Malays. **48**(6), 1179 (2019).
[24] F. A. Said, P. S. Menon, V. Rajendran, S. Shaari, B. Y. Majlis, IET Nanobiotech. **11**(8), 981 (2017).
[25] F. A. Said, P. S. Menon, S. Shaari, B. Y. Majlis, Int. J. Simul. Syst. Sci. Technol. **16**(4), 6.1 (2015).
[26] N. A. Jamil, P. S. Menon, Z. A. Noor Faizah, P. R.

Apte, ASM Sc. J. **4**, 10 (2019).
[27] Harvard Medical School "Controlling blood sugar in diabetes: How low should you go?" Harvard Health Publishing (2011).
[28] P. S. Menon, A. A. Jamil, G. S. Mei, A. R. M Zain, D. Hewak, C-C. Huang, M. A. Mohamed, B. Y. Majlis, R. K. Mishra, S. Raghavan, N. Bhat, IEEE Journ. Electron. Devices Soc. **8**, 1227 (2020).
[29] A. Belay, Journal of Lasers, Optics & Photonics **5**(2), (2018).
[30] X. Dai, Y. Liang, Y. Zhao, S. Gan, Y. Jia, Y. Xiang, Ah. S. Sens. **19**(1), 173 (2019).
[31] J. Zhu, Nanoscale Res. Lett. **4**(9), 977 (2009).

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