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SENSITIVITY STUDIES OF COPPER THIN FILM-BASED BIOCHEMICAL SURFACE PLASMON RESONANCE SENSORS

Kondankunnath Rejith Resmi*, Anagha Neerittilingal

Department of Physics, MES Kalladi College, Mannarkkad, Palakkad, Kerala, India
(Affiliated to University of Calicut, India)

Abstract: Surface plasmon resonance (SPR) sensors offer a powerful tool for label-free and real-time monitoring of biomolecular interactions and to detect very low concentrations of chemical substances. Sensitivity of these sensors can be enhanced using thin metal films for the generation of surface plasmons. Based on the thickness and quality of the metal films, minute changes in the refractive index corresponding to biochemical events can be detected. Current study focuses on the biochemical sensitivity of glucose molecules on the thin film based SPR sensors. Copper was taken as the base metallic material for the preparation of thin film for generation of surface plasmons. The nature of SPR response of this metallic film was analysed by wavelength scanning method and for various thickness. Then its sensitivity to glucose molecule was studied by simulating a glucose solution environment above the metallic film. The SPR response was recorded for change in the refractive index of the order of 0.001. By optimizing the thickness and wavelength of excitation radiation, a very high sensitivity to glucose was obtained for copper thin film based SPR sensors.

Index Terms - Sensitivity, Surface plasmon resonance, copper thin film, biochemical sensor

1. INTRODUCTION

Surface plasmon resonance (SPR) (1–4) sensors gained popularity over last few decades due to their unique physical features and characteristics that provide non-invasive method for monitoring real-time interaction with unprecedented sensitivity. It is a promising sensor technique in many fields like physical, chemical, biological, medical fields and in environment control, food security and drug research (5–8). SPR sensors detect and quantify biomolecular interactions and cancer-specific biomarkers with high precision by utilizing light-biomolecule interactions at the sensor surface (9). Coupling of surface plasmons with emitting molecules provide directionally controlled emission with emission tuning and intensity enhancements (10–12).

SPR based biochemical sensors work on the principal of generation of surface plasmons when light interact with metals. Surface plasmons are the resonant oscillations of the conduction electrons at the interface between a metal and dielectric. The presence of different modes of these collective oscillations on the surface made it an interesting tool for the investigation of surface properties(13). This is a viable method for manipulating and controlling light dispersion and propagation at the nanoscale. Resonant interaction between surface plasmons (SP) and electromagnetic radiation at the metallic contacts enhances optical near-field performance significantly (14), that made it a highly applicable technique in optics.

SPs are intensely localized over the interface and behave like electromagnetic surface waves. They propagate along the interface and diminish exponentially with distance normal to it (15). These surface waves are highly sensitive to variations in refractive index near metal surfaces in the range of surface plasmon field. This change result in a shift in the resonance wavelength of incident light or angle (16,17) . The detection of angular variations, phase relations, wavelength variations, and intensity changes are the foundations of SPR sensing techniques (18–21) . Conventional SPR sensing is based on angular variation studies in response to changes in the refractive index. Intensity-based SPR sensors are commonly used in living cells owing to their smooth functioning, rapid imaging, and simple optical setup. However, it suffers from a limited dynamic range. SPR phase interrogation methods on measuring the change in the phase of the reflected light at the metal-dielectric interface where surface plasmons are excited. But this method often requires more complex and expensive optical components compared to other methods. The wavelength interrogation approach, in contrast to the other SPR methods, offers a wider dynamic range, superior sensitivity and provides motion less technology (22).

In the current research work, initial studies were focused on the optimisation of the parameters of copper (Cu) thin film for getting a very good SPR response. By wavelength tuning method, the excitation wavelength suitable to Cu metal thin film for ideal SPR curve was analysed. Then the thickness of the film in nanometer range was optimised. After these optimisations, its sensitivity to the glucose biomolecule was analysed by simulating a glucose solution environment above the thin metal film. The shift in the SPR reflection dips were analysed for various concentrations of glucose solution by varying the refractive. The intensity of reflected lights and the full width at half maximum (FWHM) of the reflection curves were analysed. The angular sensitivity of the thin film Cu based SPR sensors was studied to bring out its potential advantages over conventional metals like gold or silver.

2. METHODOLOGY

SPR studies were conducted on metal thin metal film of copper (Cu) in the nanometer range. Kretschmann Raether configuration based on attenuated total reflection method was used for the analysis of SPR response (23). In this method, the light passes through the prism and get reflected at the base of the prism. The metal film is attached at the base of the prism, with air as dielectric above the metal as shown in figure 1.1. Thus, light get reflected from the three-layered structure (prism-metal-dielectric). For the analysis of this N-layered structure, Transfer matrix method model (TMM) was employed (24). The reflected light intensity can be calculated using Fresnel equations and relevant boundary conditions.

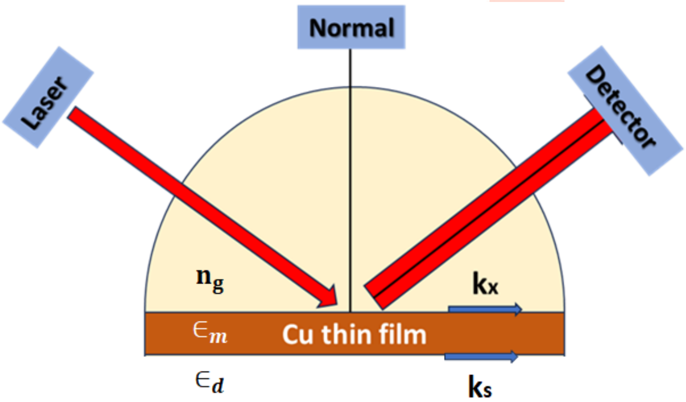

Fig.1.1. The SPR analysis set up based on Kretschmann Raether configuration

During the analysis, the angle of incidence of the incident light on the metal surface is gradually increased so as to find the angle of Total Internal Reflection (TIR). Above the TIR angle, due to the presence of evanescent waves, surface plasmons are generated. When the incident angle (θ_i) matches the SPR angle (θ_s), the incident light gets absorbed, producing a sharp dip in the reflected light intensity. Absorption of light by the surface plasmon at the metal-dielectric interface occur when the wave vector of the incident light (k_x) through the prism matches surface plasmon wave vector (k_s). The equation relating the angle of incidence of light and the wavevector (k_x) (25) is given by:

$$k_x = k_0 n_g \sin\theta_i \quad (1)$$

Where k_0 is the free space wave vector, n_g is the refractive index of the glass prism. The relation connecting k_s and dielectric functions of the metal (ϵ_m) and dielectric medium (ϵ_d) is given by:

$$k_s = k_0\sqrt{\frac{\epsilon_m \, \epsilon_d}{\epsilon_m + \epsilon_d}} \quad (2)$$

SPR absorption takes place when the light wave vector is equal to the surface plasmon wave vector

$$k_x = k_s \quad (3)$$

In the current research work, simulation analysis was done using the software WINSPALL. Using this software, SPR reflection curves were modelled by providing appropriate refractive indices for metal and dielectric material. Both angular scanning (AS) and wavelength scanning (WS) interrogations were conducted for the thin metal film of Cu. In AS, the SPR curves were generated by keeping the wavelength fixed while in WS, SPR curves were generated by varying the wavelength. Optimisation of the thickness of the thin film in the nanometer range was also carried out for getting ideal SPR response. The simulation method was extended for the investigation of biochemical sensitivity of this nanometallic thin film. A glucose solution model was adopted above the metal layer, and the AS and WS analysis were carried out. By changing the concentration of glucose solution, the SPR studies were conducted for Cu metal thin film and its sensitivity was analysed

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3. RESULTS AND DISCUSSION

3.1 SPR Studies Copper thin film

SPR reflection dips were generated via simulation for metallic thin film of copper with an arbitrary 50 nm thickness. Initially wavelength interrogation method was carried out in the visible range from 450 nm to 750 nm in steps of 50 nm and the results are shown in the figure 1.2.

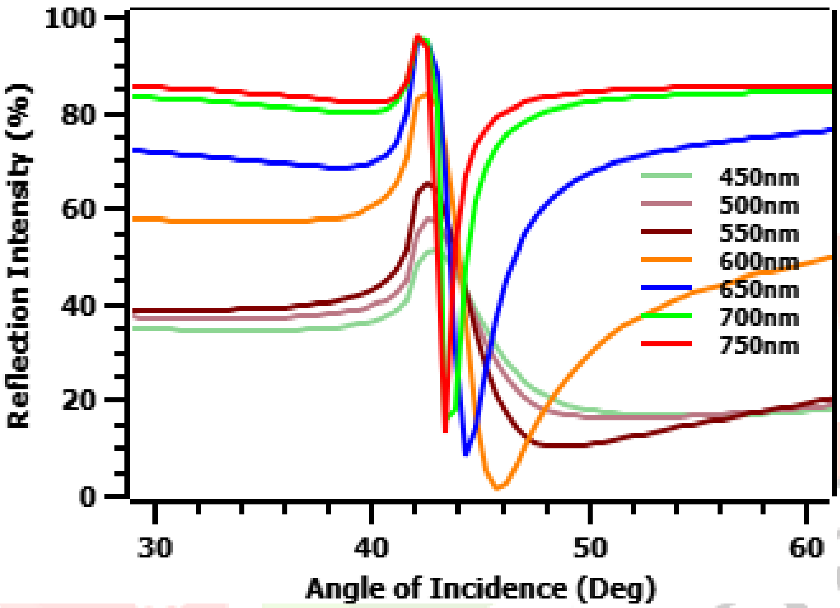
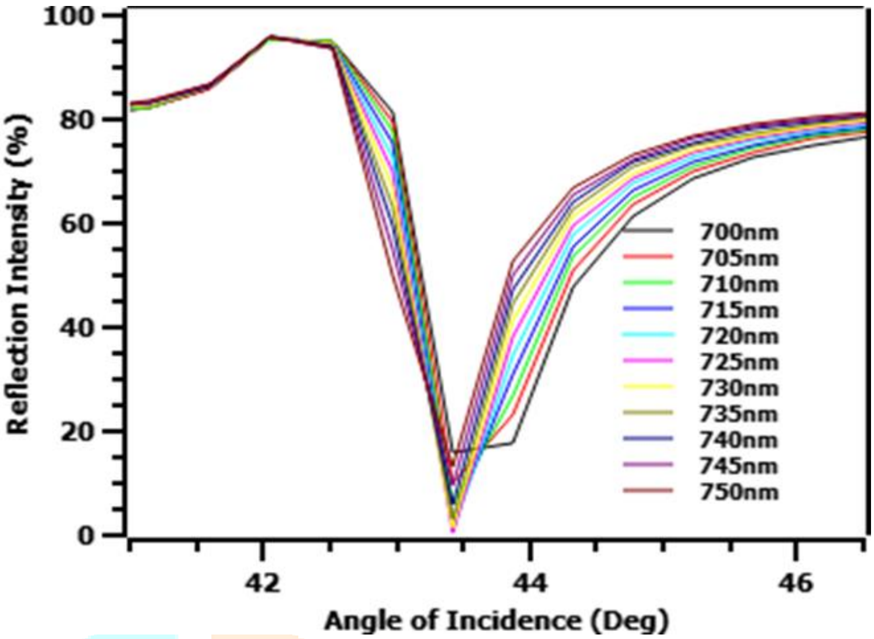


Fig. 1.2. SPR curves for Cu thin film via wavelength interogation method in visible range

The figure shows variation in the reflection dips with change in the excitation wavelength. The percentage of reflected light intensity and the FWHM of the curves also changes. An approximately ideal SPR curve was



obtained for wavelengths 700 nm and 750 nm, in

Fig. 1.3. Fine tuning of SPR response in the visible range for getting sharp dip curve.

the high wavelength region of visible light. The process repeated for fine tuning the wavelength in this range for getting sharp SPR response by increasing the wavelength in steps of 5 nm. The result is shown in the figure 1.3. All the curves had almost same SPR angle, but the intensity of reflected light and FWHM varied with change in the wavelength. The finest curve obtained was for the wavelength 725 nm and with SPR angle 43.48^{o} and FWHM 0.96^{o}. The study continued for finding the optimum thickness of the Cu film by fixing the excitation wavelength at 725 nm. The thickness changed from 10 nm to 90 nm, results are shown in the figure 1.4. The results show that with the change in the thickness, the intensity of reflected light varies, also the FWHM of the SPR response. The finest SPR response was obtained for the Cu film of thickness 40 nm, with almost all radiation get reflected. SPR angle was 43.48^{o} with FWHM of the curve 0.57^{o}.

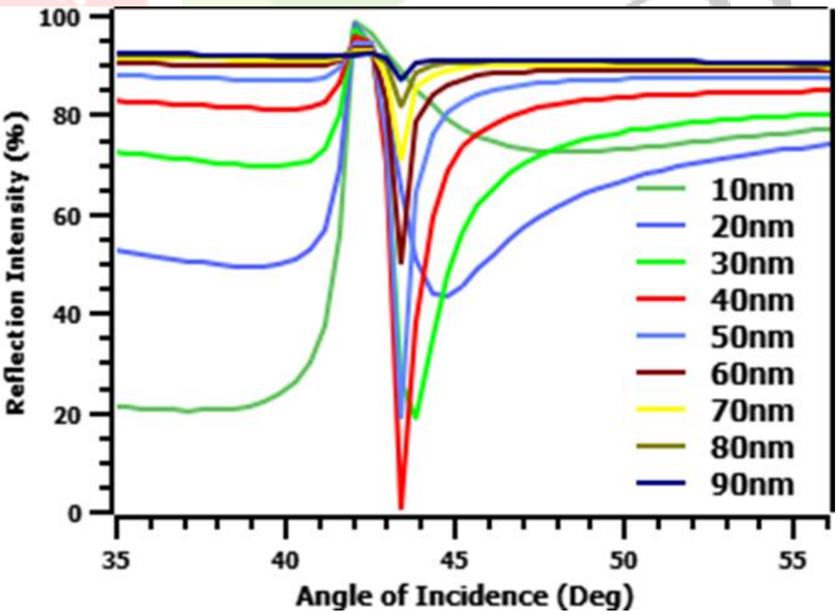


Fig. 1.4. Thickness variation studies of Cu thin film at 725 nm wavelength

3.2 Biochemical sensitivity of copper thin film

After optimising the conditions for getting Ideal SPR curve from the Cu thin film, the analysis continued for understanding the biochemical sensitivity of this thin Cu film based SPR sensor.

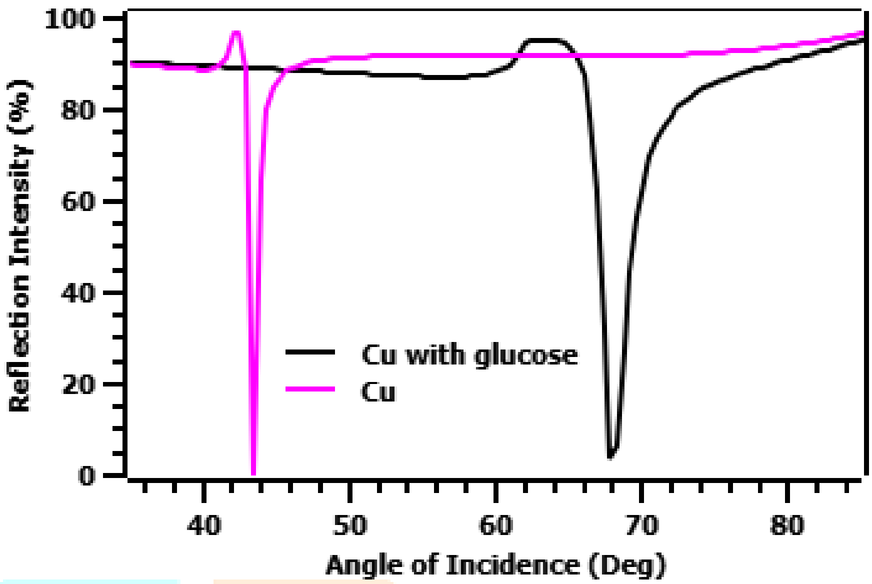


Fig. 1.5. SPR response of Cu thin film-based sensor to glucose

Due to protentional importance of glucose as a biochemical substance, its solution in water was taken as the substance for testing the biochemical sensitivity of Cu thin film based SPR sensor. The refractive index of glucose solution varies with variation in its concentration in water. For the current study, 1% glucose solution was taken and its refractive index was determined as 1.321, by conventional prism-based experiment using Snell's law. This glucose solution environment was simulated above the Cu thin film and its SPR response was analysed using WINSPALL software. The result was shown in the figure 1.5. A drastic angular shift in the SPR response was noted, as SPR angle shifted from 43.48º to 67.74º. This angular shift signifies that SPR sensor based on Cu thin film is very sensitive to changes in the environment, enabling it to detect the presence biochemical substance like glucose. This behaviour exemplifies the potential application of Cu thin film in the nanometer range as optical sensor for glucose monitoring.

The analysis continued for understanding the SPR response of this sensor with minute changes in the refractive index. For this study, there made a change in the refractive index (RI) of the order of 0.001 and the reflection dips were analysed. The results are shown in the figure 1.6. A small change in the concentration of glucose solution, will make changes in its refractive index. The results here show a significant change in the SPR angle with change in the refractive index of the order of 0.001. With increase in the RI, the dip angle also increases. The sensitivity $S_\theta=\Delta\theta/\Delta n$ is shown in the table 1.1. The biochemical sensitivity curve for Cu is shown on the figure 1.7. The straight line in the figure shows, the increase in the biochemical sensitivity of thin Cu film based SPR sensor, with increase in the concentration of the material above the metal film.

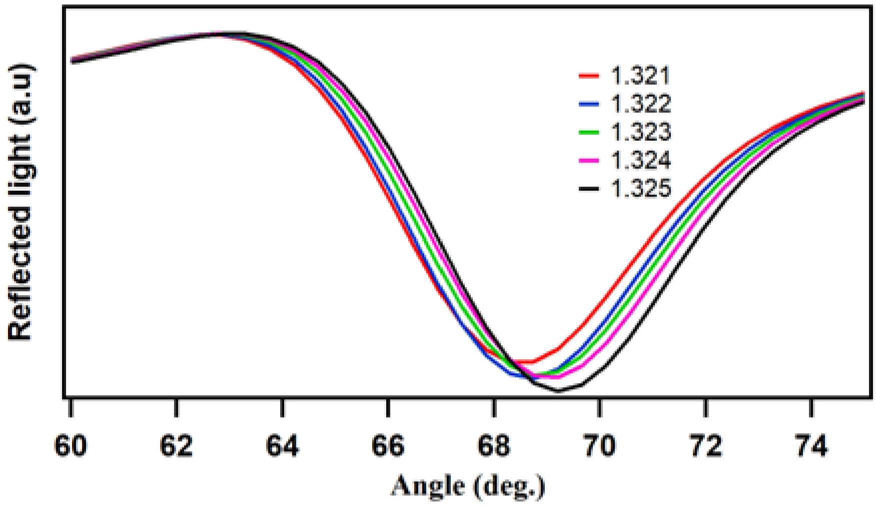


Fig. 1.6. The shift in the resonance angle with minute changes in the RI of glucose on Cu thin film based SPR sensor

Table 1.1: The sensitivity of Cu thin film based SPR sensor to glucose

Refractive Index (RI)	SPR angle (Deg.)	Sensitivity (S_θ)
1.321	67.74	180
1.322	67.92	220
1.323	68.14	210
1.324	68.35	210
1.325	68.56	

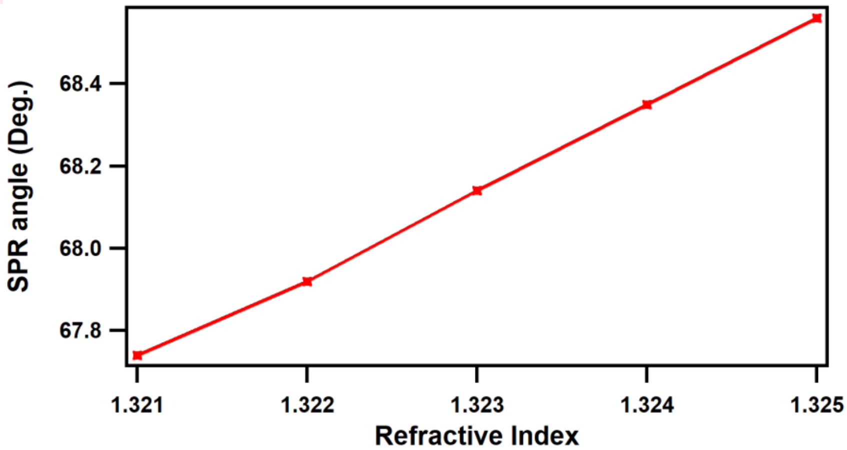


Fig. 1.7 Variation in the SPR dip angle with changes in the RI

4. CONCLUSION

The SPR studies based on Cu thin film in the nanometer range was carried out via simulation analysis. In the current research work, optimisation of the parameters of metallic Cu thin film for getting ideal SPR curves were analysed. By wavelength interrogation method, the wavelength for the maximum excitation of the surface plasmons were determined. Then by fixing the wavelength, the thickness of the thin film for getting a very good SPR dip was analysed by examining the intensity of reflected light and by measuring the FWHM of the curve. The Cu thin film showed its maximum SPR response at 725 nm with 40 nm thickness. The analysis continued for the biochemical sensitivity of this thin film based SPR sensor with glucose as the material for study. A drastic shift (~24°) in the SPR angle, for a small concentration of the glucose solution on this metallic surface shows its adaptability as a good SPR sensor. Also, it showed shift in the resonance angle with minute changes in the refractive index of the order of 0.001. This makes the Cu thin film based SPR sensor in the nanometer range as a very good alternative for conventional gold or silver based SPR sensors, in terms of cost as well as sensitivity. The sensitivity of the order 10^3 to the presence of glucose clearly find its potential applications particularly in the medical field, making it promising SPR tool in the near future.

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