Magnetoplasmonic Materials for Applications in Biosensing

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Cheap biosensors designed for quick detection of a variety of biomarkers are critical for efficient point-of-care treatment, diagnosis of diseases in developing countries and fast turnaround times for genetic mapping.[1] Ideal biosensors operate with limited sample volume, be able to detect multiple biomarkers at the same time, and have a very low limit of detection (LOD). Surface plasmon resonance (SPR) based biosensors employ a sensing strategy that can achieve a very low LOD without the need to employ a labeling molecule, and when properly engineered can operate with a very low sample volume and are capable of detecting multiple analytes in a label free way. The first SPR based sensor was described in 1983 as a way to detect changes in gas composition.[2] Advancements in nanotechnology, nanofabrication, and microfluidics has brought these devices to the forefront of sensor technology.[3] Magnetoplasmonic materials provide the next step in improving the limits of detection even further, and opening a new frontier to explore.

SPR based sensors are typically employed in the Kretschmann configuration, where light is reflected off a thin layer of plasmonic material.[4] The plasmon will be excited if the light matches the plasmon's momentum, then the reflected beam carries information about the resonance to a detector. The plasmon resonance condition depends on the refractive index of the media in contact with the device. Changes in the refractive index of the media close to the device's surface will affect the coupling of the light to the surface plasmon.[5] Chemical sensing relies on detecting a change in the coupling characteristics between the interacting light and the plasmon resonance, such as measuring a change in the coupling angle or wavelength, or by measuring a change in the phase, intensity, or polarization of the light.[6] SPR devices can be characterized by figure of merit (FoM) values, which is the refractive index sensitivity divided by the plasmon resonance linewidth. A recent design achieved a FoM of 108, which is nearly the theoretical limit for SPR devices.[7] Magnetic materials can accentuate the sensing characteristics of SPR based devices by exploiting magnetic effects, achieving greater sensitivity, and a higher FoM. Simple devices can employ an effect known as the Transverse Magneto Optical Kerr Effect (TMOKE), where a magnetic field perpendicular to the direction of the reflected beam and parallel to the thin film shifts the plasmon resonance. Alternate signs of the magnetic field induces opposite shifts in the plasmon resonance. Taking the difference between these signals produces a derivative-shaped feature centered at the

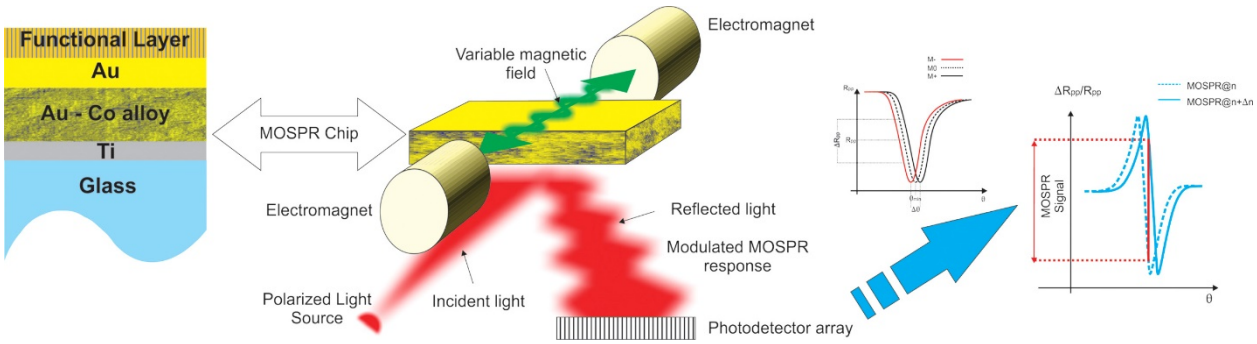

Figure 1. Left: An example device made of a Au/Au-Co alloy/Ti trilayer. Center: The device configuration with the magnetic field applied parallel to the sensing surface. Right: The alternating magnetic field induces a shift in the plasmon resonance. The difference between the two shifted signals produces a sharp, derivative shaped feature.[9]

plasmon resonance, as illustrated at the right in figure 1. A shift in this feature (e.g. due to a change in the refractive index) will be more pronounced than a similar shift in the plasmon resonance, allowing greater signal-to-noise ratios and lower limits of detection.

Magneto-optical surface plasmon resonance (MOSPR) based devices can be as simple as a ferromagnetic material layered on a plasmonic material. One implementation of this by Grunin et al. is a Ag/Fe/SiO2 trilayer, where the initial iron layer is sputter coated onto a glass substrate, followed by a sputter coated silver layer. Functionalizing the surface of the Ag allowed selective binding to biological agents. This study explored a variety of films with different Fe thicknesses. Optimal sensitivity was achieved by balancing magneto-optical activity with optical losses, and found that minimizing optical losses was the most important factor. A 100 nm thick silver layer with a 5 nm thick Fe layer performed the best. A 10 nm SiO2 layer insulated the Fe from the aqueous media. They demonstrated this device with a series of glycerol solutions with known refractive indices. This setup could be applied as a normal SPR based sensor, or as a MOSPR sensor with the application of a magnetic field, allowing direct comparison between the different detection modes. They found that the MOSPR based sensor had a 3 times higher sensitivity compared to when the device was employed as an SPR sensor (1780 Refractive Index Units^{-1} vs. 500 RIU^{-1}), and had a 4 times lower limit of detection (0.00056 RIU vs. 0.002 RIU). These results were matched by a study by Manera et al. where a Au/Co/Au trilayer exhibited two times the enhancement in sensitivity when employed as a MOSPR sensor compared to an SPR based device.

A more recent MOSPR design employs a cylindrical nickel pattern as a magnetoplasmonic nanoantenna.[10] The nickel nanodisks are patterned on by coating a glass surface in polystyrene beads, and depositing a mask around the beads. Mechanical exfoliation of the beads leaves circular holes that Ni was sputter coated onto. Removing the mask left a pattern of Ni nanodisks. Instead of measuring a wavelength shift in the plasmon resonance, this configuration relied on a change in the reflected light's polarization, as shown in figure 2. The probing light source is initially p-polarized, but a magnetic field perpendicular to the plane of the device induces an elliptical polarization based on the light's interaction with the SPR. Measuring the magnitude of polarization and taking the difference of the oppositely magnetized signals, similar to TMOKE analysis, gives a very accurate measurement of the plasmonic resonance peak. This sensor demonstrated an FoM approaching 150 for 100 nm Ni nanodisks when measured with glycerol solutions. This FoM is greater than even the theoretical limit for SPR based devices.[7] With advanced polarimetry tools, the authors estimate a detection limit of a few zettagrams/nanodisk. This study offered a practical, cost effective implementation that doesn't rely on noble metals or complex nanopatterning processes. The authors note that a film of Au on top of the nanoantennas could improve the performance even further.

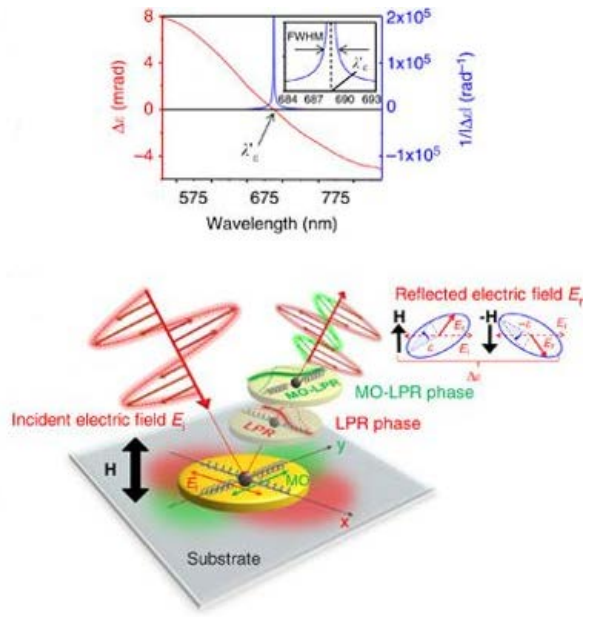

Figure 2. The reflected light will have an induced elliptical polarization based on its interaction with the surface plasmon.[10]

Biosensors based on magneto-optical effects offer greater limits of detection and sensitivity, but they are limited by cost and stability. MOSPR based

devices typically rely on noble metals, which have low earth abundance and are expensive. The sensing instrumentation is also very complex, which will make it difficult to incorporate in point-of-care workflows. Stability can is be a limiting factor. One study found significant corrosion in as little as 30 minutes of a typical Au/Co/Au trilayer device immersed in saline buffered solution.[9] The last hurdle to overcome is the need to detect multiple analytes in a complex solution. These barriers need to be overcome before these sensors can find practical applications.

Magneto-optical based plasmonic devices make excellent use of Kerr effects to dramatically enhance the performance of biosensor detectors. By employing common magnetic materials, sensors can achieve much greater levels of sensitivity and limits of detection compared to devices that rely solely on surface plasmon resonance for detection. Further development in this area will need to focus around the practical limitations in implementing the technology, including finding a way to analyze complex media, such as human serum, and crafting devices in a cheap, portable manor.

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