Summer 2015

Surface Plasmon Resonance Enhanced Ellipsometry for Biodetection

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Introduction

Biosensors enable scientists to learn more about biomolecular interactions, and are often used as detectors to indicate the presence of specific analytes. Currently, many detection methods require what are called labels, molecules that bind to an analyte of interest and can be easily detected. Radioactive isotope methods are often used for this purpose, but labels such as these have the potential to interfere with the processes and molecules being studied. This poses a problem for medical screening, as labels may lead to an incorrect diagnosis. Therefore, label-free bio sensing techniques are in demand. Surface Plasmon Resonance Imaging (SPR), is one such method. A phenomenon derived from Maxwell’s Equations, SPR occurs at the interface between a dielectric and a metal thin film (Fig. 1). In the metal surface, electrons are not tied to particular atoms and are free to move throughout the material. This “sea” of free electrons can be modeled as a simple harmonic oscillator. In the presence of a drive force—in this case, the electric field in a light wave—electrons will oscillate. Unless the drive force is very close to the resonance frequency, little energy will be transferred to the oscillator. If the driving force matches the resonant frequency however, total energy transfer and SPR will occur. In other words, when a light beam has the correct wavelength to excite the plasmon, it will be absorbed by the metal.

One important property of SPR is that the resonant frequencies can be found in the visible light spectrum. The particular frequency required depends largely on the dielectric constant of the metal used. Most importantly, this constant is sensitive to the refractive index of the metal’s surroundings. Consider a glass-gold interface submerged in water (Fig. 1). This system will oscillate at some frequency. If foreign particles are introduced, they alter the refractive index of the water and redshift the plasmon frequency. Thus, the plasmon surface can “detect” refractive index changes and foreign particles with high levels of sensitivity.

Methods

Ellipsometry is a method of examining material surfaces by reflecting linearly polarized light off of them. In an ellipsometer, light of the desired frequency and polarization angle is focused onto the surface at a chosen angle of incidence. Linearly polarized light can be modeled as the sum of two waves: a s-wave perpendicular to the plane of incidence and a p-wave in the plane of incidence. In linear polarizations, these two waves are in phase with each other. However, the s and p waves do not interact with surfaces in exactly the same ways, and they are phase shifted in the reflected beam, resulting in elliptically polarized light (Fig. 2). The ellipsometer’s detector picks up the outgoing light and measures two parameters: \( \Psi \) and \( \Delta \). \( \Psi \) is a quantity proportional to the intensity of the beam and \( \Delta \) is the phase shift between s and p waves. These parameters are related by our WVASE software using Fresnel’s Equations, and with proper technique, we can fit our experimental data and model the surface layers of the sample. The Kretschmann Configuration (Fig. 3) is a scheme that was devised to combine the capabilities of the ellipsometer with the sensing potential of SPR. It requires that the ellipsometer be set at a 90 degree angle of incidence. The beam then travels into a dough prism, is totally internally reflected off the top face, exits the prism, and enters the detector. At the location where the light is totally internally reflected, we place a gold film sample slide, using anisole as a glass refractive index matching fluid (fig. 4). Theoretically, none of the light should exit the prism. However, due to peculiar properties of light that are analogous to the more familiar electron tunneling phenomenon, the light enters the gold and can excite plasmons. The ellipsometer allows us to test every wavelength in the visible spectrum and to find the resonant frequency, which appears as a dip in the graph of \( \Psi \) vs wavelength. Because \( \Psi \) is related to the reflected light intensity, it drops dramatically at the resonant frequency since that light is absorbed and not reflected.

Results

Sample Characterization and Calibration

The ~60 nm samples generally resulted in the best coupling compared with 40 and 100 nm samples (fig. 5, left). Of the ~60 nm samples, 60A had by far the best plasmon coupling (fig. 5, right). Upon calibrating this sample with 10, 20, 30, 40, and 50 percent glycerine solutions (fig. 6), it was determined that the technique could theoretically detect refractive index changes to six decimal places. Plasmon red-shifting was clearly observed (fig. 7). Actual resolution has not yet risen to the theoretical level, but it continues to improve as the equipment and techniques are optimized. Nanogold samples (~5-10 nm) were also tested (not pictured), but the localized plasmon showed no detectable redshift.

Model

WVASE Model fitting of sample 60A calibration data is shown below. The preliminary generated model (not pictured) shows all of the major features of the experimental data, including an intensity dip in the visible spectrum that redshifts as the refractive index of the cauchy layer is increased. Layers of the model that still need optimization include the refractive index matching fluid layer, as well as the gold and titanium layers, which are currently being modeled by oscillator functions.

Glucose Detection

The SPR technique showed some promise of distinguishing between glucose concentrations. A linear fit to the data from several concentrations yields a slope near the expected value (fig. 8). However, there is a large systematic error causing the intercept of the graph to be incorrect. For true concentration identification, the technique would need to be further optimized to remove this systematic error, as well as large random errors. While it was difficult to pinpoint exact concentrations of glucose with this technique, it proved to be a useful tool for detecting the presence of glucose in small concentrations. Errors were reduced by using a large number of trials. A method involving the repeated alternation of solution and water yielded positive results for the detection of 10 mM concentrations (fig. 9).

Gas Detection

No positive results have yet been achieved for the detection of various atmospheric gases. However, once a better fluid pumping system and a complete computer model are developed, gas sensing may be feasible.

Discussion

Over the course of this project, the Ellipsometer and its accompanying software, WVASE, were successfully adapted to function as an SPR detector. Sample calibration and glucose detection data confirm that the device can be used to detect foreign particles in water. After further optimization, the ellipsometer may be ready for biosensing experiments. Plans for optimization include building a fluid pumping system and evaporating gold directly onto the prism instead of onto a slide. Both of these changes combined would eliminate sample mounting from the procedure, which would drastically reduce errors and increase day-to-day consistency of experimental data. Gold evaporation onto the prism would also eliminate several intermediate sample layers, reducing scattering and potentially increasing coupling strength. An air tight pumping network would have the added benefit of improving sample cleaning.

Acknowledgments

A special thanks to Dudley Thomas of the Kenyon College Chemistry Department for help with chemical handling and safety.

Key References
