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SURFACE PLASMON RESONANCE DESIGN OF CHIP-TYPE SENSOR WITH NANOPARTICLES

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Abstract. *The heterogeneous character of thin gold films prepared by thermal evaporation and the dependence of this heterogeneity on the rate of their deposition must be considered when exploiting their optical properties for biosensor purposes. Such is the case for the performance of thin gold films for surface plasmon resonance (SPR) biosensors. SPR is a phenomenon occurring at metal surfaces (typically gold and silver) when an incident light beam strikes the surface at a particular angle. The main goal is to develop a theoretical model and measuring setup for nanotechnologies, which can be used to fabricate Au nanoparticles for possible SPR biosensing applications. Care must be taken in preparing film with a high fraction of gold (>95%) or it may be drastically degraded. MEMS (Micro-Electro-Mechanical Systems) technologies have provided a wide spectrum of new designs and fabrication techniques for microsensors, micro-fluidic systems and micro-systems. However, the search for additional biomedical applications is the driving force behind the continuous growth of SPR technology. This paper discusses the basic concept of bi-directional flow rate detection, design and fabrication of a chip-type SPR sensor, which can be used to monitor biomolecular interactions.*
Keywords: Chip-type, Nanoparticles, SPR

1. **Introduction.** The most common means of surface plasmon resonance excitation is achieved through the Kretschmann configuration, as shown in Figure 1. This configuration depends on the attenuated total reflection in order to excite SPR. To induce surface plasmon resonance, a specific incident angle of light with respect to the metal-dielectric interface must be achieved. Traditional SPR sensor systems utilize a metal film deposited on a bulk prism, and use an optical phenomenon in which incident light excites charge density waves at the interface between the metal and a dielectric [1-3]. The resonance angle at which the coupling of the incident light and the surface plasmon waves occurs is measured at the minimum reflection intensity. Optical surface plasmon resonance (SPR) devices, which were introduced as possible chemical sensors more than 30 years ago, became an actual commercial system in the beginning of 1990 [1]. Chemical sensors based on the SPR phenomenon were studied initially in the so-called Kretchmann configuration [2], in which the sample is deposited on the metal-coated surface of a right-angle prism. There are different models to interpret the SPR response of gold films prepared by thermal evaporation, and the interpretation of the SPR curves requires that both a global heterogeneity of the gold films and a surface roughness be considered.

Light at an opportune wavelength is impinged in the prism in order to induce surface plasmon resonance [2,3] on the thin metal film. Variation in the light incident angle yields

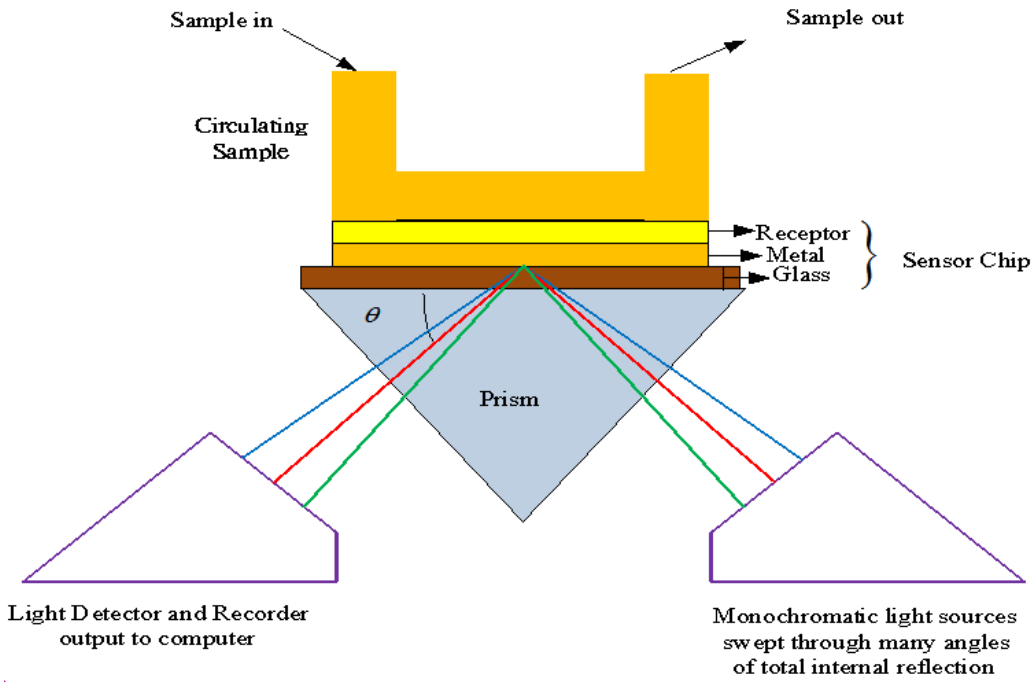

FIGURE 1. Standard Kretschmann configuration of attenuated total reflection

an SPR response curve that can be studied to evaluate quantitatively several optical properties of the sample. Moreover, monitoring the reflected light at a fixed angle requires a highly sensitive tool in order to study in real time any tiny optical modifications occurring on the sample.

A typical example of the use of an SPR device is to monitor the thickness of a specific chemical deposited on the sensor. The realization of DNA tips or other specific sensors are generally based on this concept: a chemical ligand is fixed on the metal-coated face of the prism, and then the analyte flows over and binds the ligand creating a thicker layer that can be sensed as a tiny difference of index of refraction [4-7].

To induce surface plasmon resonance, a specific incident angle of light with respect to the metal-dielectric interface must be achieved. At angle θ_{sp}, the electromagnetic wave interacts with the electrons at the metal-dielectric interface and generates a surface plasmon. The relationship is

$$k_{sp} = k n_p \sin \theta_{sp} \tag{1}$$

θ_{sp} is the angle needed to generate a surface plasmon, k_{sp} is the wave vector of the surface plasmon, the wave vector of the bulk electromagnetic wave is k, and n_p is the refractive index of the glass prism. We note that Kretschmann geometry is only used to excite surface plasmons on planar or flat surfaces along a metal-dielectric interface. In the case of metallic nanoparticles, SPR is achieved differently; since the oscillations are localized, the wave vector k_{sp} is not needed. Consequently, surface plasmons related to metallic nanoparticles are termed localized surface plasmons.

The basic principle of SPR is a quantum phenomenon in a thin-film structure. The metal surface electrons are excited by an electromagnetic wave (visible light or UV) under a special incident angle to meet the resonance condition [9-12]. This detection method is highly sensitive to the surface refractive index, and it is a very sensitive tool for verifying the surface properties. The necessities of a successful high sensitivity SPR sensor for biochemical applications are affected by two basic factors:

(1) SPR allows the measurement of the kinetics of biomolecular interactions in real time with a high degree of sensitivity.

(2) Labeling of the biomolecules is necessary for their detection. These features will allow for applications in biomedicine, biochemical measurement in pharmaceutics, environmental monitoring, the food industry and agriculture in the near future.

2. SPR Sensor Configuration.

2.1. **Surface – Prism.** An apparatus known as a Kretschmann prism is often used for SPR sensors, which use a prism to couple some of the light to the SP film and reflect some to an optical photo detector [13]. A biological sample is placed on the metal film surface. As this layer changes, the refractive index of the metal film/bio sample pair changes, causing less (or more) light to strike the photo detector. The Kretschmann prism itself is the prism in the center of a detection apparatus. If a prism is coated with a material with an infinitely high index of refraction, total internal reflection occurs for all light reflected past some critical angle and all the light sent toward the surface is reflected away from the surface. This model of how total internal reflection works is so good that it is used for making most common optical instruments, from binoculars to lab equipment. However, when light is totally internally reflected off the inside of a prism, there is a probability that some of the light will exist outside the surface of the prism. This light is called the evanescent wave. Instead of coating the prism with a material that approximates an infinite refractive index and thus allow for almost no evanescent wave, the prism is attached to a sensor chip with a thin layer of metal. There are waves in the sea of free electrons in the metal. This motion of electromagnetic waves in the surface of the metal is called the surface plasmon. When the surface plasmon has similar properties to the evanescent wave, the couple are as follows:

$$r_{123}(\theta) = r_{12}(\theta)\frac{1 + r_{12}^{-1}(\theta)r_{23}e^{(\theta)d_2}}{1 + r_{12}(\theta)r_{23}e^{(\theta)d_2}} \tag{2}$$

$$r_{ab}(\theta) = \frac{\varepsilon_b k_{az}(\theta) - \varepsilon_a k_{bz}(\theta)}{\varepsilon_b k_{az}(\theta) + \varepsilon_a k_{bz}(\theta)} \tag{3}$$

where $r_{ab}(\theta)$, a and $b = 12$ and 23, is the amplitude coefficient of reflection from region a into region b; $k_{z2}(\theta)$ is the wave number along the direction normal to the metal-dielectric interface; and d_2 is the thickness of region 2 (metal). The total reflectivity of the three-layer system is

$$r_{123}(\theta) = |r_{12}(\theta)|^2 \left|\frac{1 + r_{12}^{-1}(\theta)r_{23}e^{(\theta)d_2}}{1 + r_{12}(\theta)r_{23}e^{(\theta)d_2}}\right| = \frac{1 + 2De[r_{12}^{-1}(\theta)r_{23}(\theta)]e^{(\theta)d_2} + [r_{23}(\theta)]^2 e^{(\theta)d_2} \ldots}{1 + 2De[r_{12}(\theta)r_{23}(\theta)]e^{(\theta)d_2} + [r_{23}(\theta)]^2 e^{(\theta)d_2} \ldots} \tag{4}$$

2.2. **Nanoparticles.** Gold nanoparticles can be fabricated under solution condition, and the optical scattering effect comes from surface plasmon resonance. The optical property is influenced by the wavelength of the incident light and particle sizes. In this research, the nanoparticles were fabricated by gold tri-chloride and a reducing agent, with sizes from 10 to 100 nm.

The nanoparticles must absorb on a substrate for a chip-type sensor. The sensor chip contained four sensing sites, which were fabricated by MEMS technology. The chip material was polymer combined with glass chips, and a layer of gold was deposited as the energy conveying layer [15]. The nanoparticles absorbed onto the sensor chip by the electric field driving method, which could precisely control the quality and quantity of the

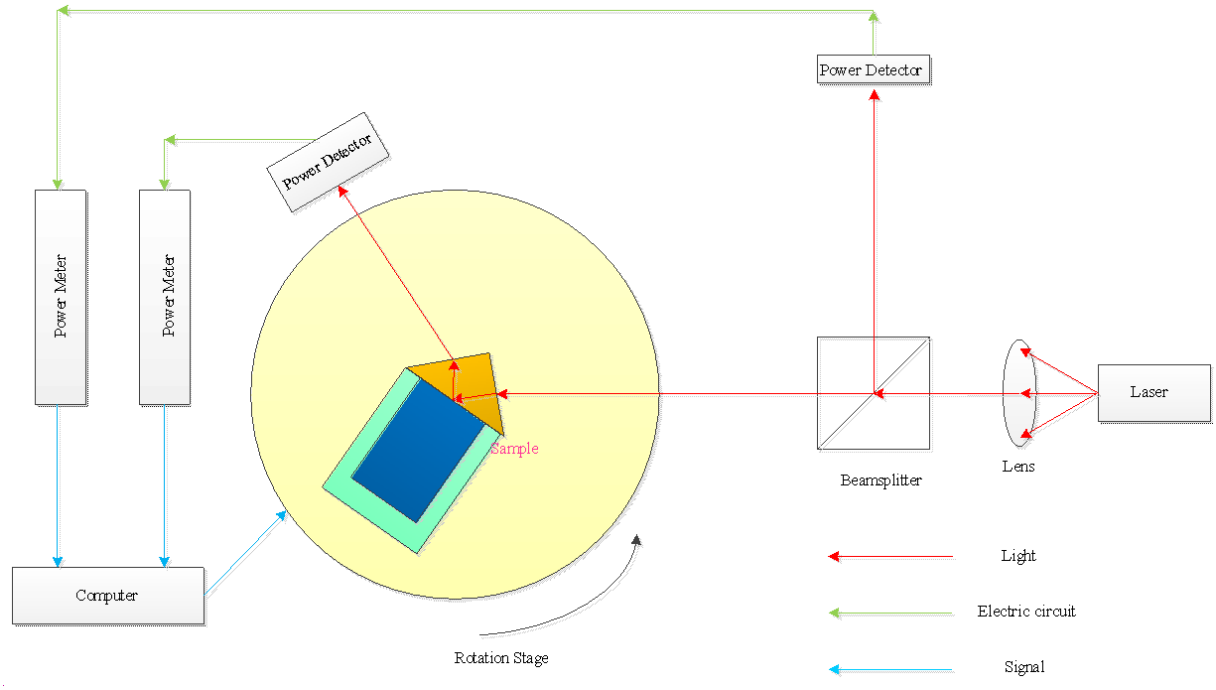

FIGURE 2. Optical set-up for SPR reflectivity measurements

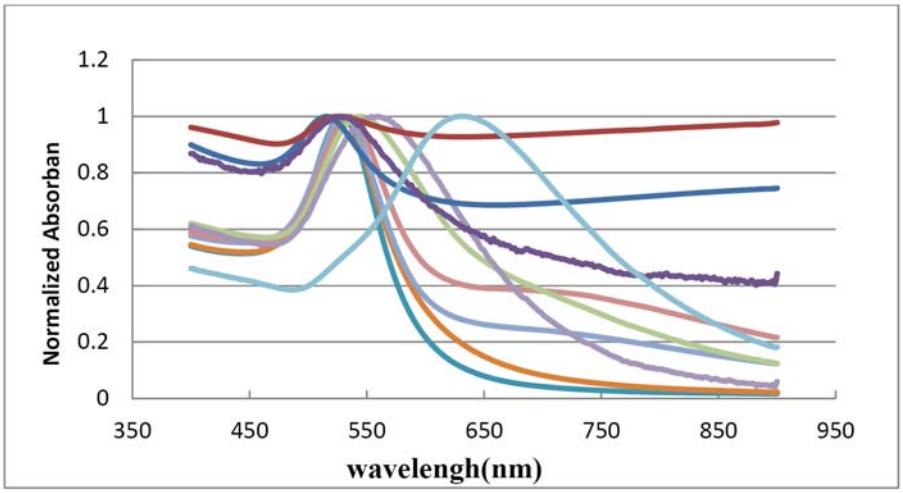

FIGURE 3. Absorption spectrum

surface particle layers. In the experiment, the particle sizes were measured by optical transmission and scattering methods.

Actually, the size can be estimated by the naked eye; the color and size have a positive relativity. The sensor was successfully fabricated by the MEMS process, and the electrochemical properties could be easily monitored by the amperometric method to control the sensor surface quality and biomedical molecules absorption, as shown in Figure 3.

This research combined optical, chemical, electrical and biomedical fields, which was a challenging task. The method, as described, will be used to monitor nanoparticle and biomedical materials, which have an enormous potential in clinical uses. The portable biochemistry analyzer will be investigated using a similar detection method.

Biotechnology is the key to the next generation of industrial technology, but many related technologies must be integrated to speed the research in this field. Fortunately,

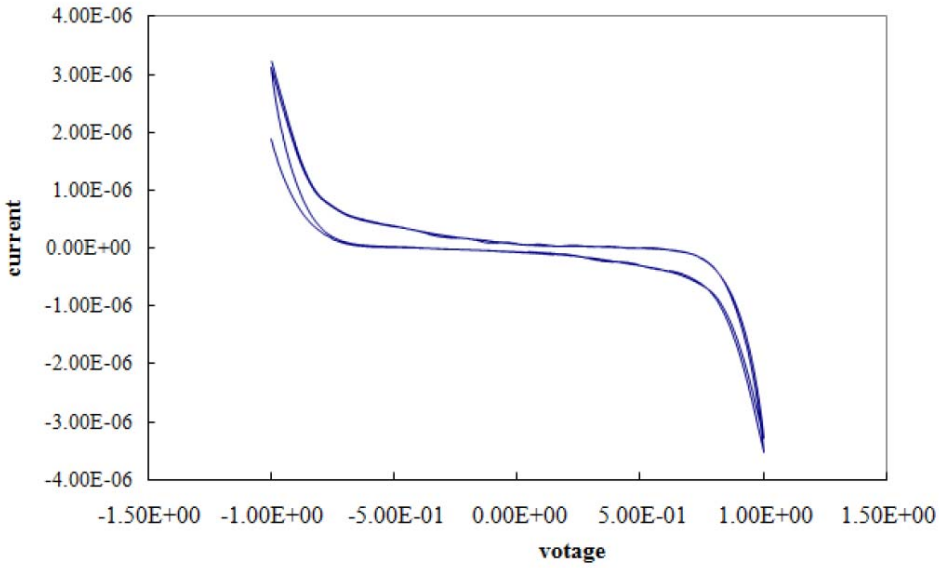

FIGURE 4. Electrochemical process

mature semiconductor technology can be used to miniaturize the size of the sensing element.

The electromagnetic approach is derived from the superposition of the incident and scattered electromagnetic fields when these fields interact with the transition moment of a molecule near the surface of a metallic particle. Localized field effects from the metallic particle strengthen the electromagnetic fields near the surface as shown in Figure 4. Recall that the cross-section of Raman scattering requires that the transition moment be raised to the fourth power and that the magnification of the electromagnetic field can increase the scattering substantially. Using this information, Franzen derived an equation for the Raman scattering cross-section:

$$\partial_R = \frac{8\pi\omega_X^3\omega_0 M_{if}^4}{9h^2c^4}\left(\int_0^\infty (f|i(t))\exp\left\{i(\omega_i+\omega_0)t-\Gamma t\right\}dt\right) \tag{5}$$

3. Detection Method.

3.1. **Surface plasmon resonance.** Surface plasmon resonance is the quantum phenomenon which happens between the metal surface and the dielectric interface. The electrons are excited by the electromagnetic waves, which causes a resonance condition. The amplitude of the resonance condition is attenuated by the environment materials. It is a very sensitive method used to determine the refractive index around the sensing sites. The electric field wave vector in the TM polarized direction comes from the incident light, which can be presented as affiliations [16]:

$$k_i = \frac{2\pi n\sin(\theta)}{\lambda} \tag{6}$$

where n is the refractive index of the material, λ is the wave length of the incident light, and θ is the incident angle of the light. When the wave vector of the light is equal to the material wave vector, the resonance condition happens. The wave vector of the material can be calculated by the following formula:

$$k_{spw} = k_0\sqrt{\frac{\varepsilon_s\varepsilon_m}{\varepsilon_s+\varepsilon_m}} \tag{7}$$

The resonance condition can be procured by angle and wave length modulations. The electric field strength exponentially decays due to the penetration depth increasing. The characteristic decay length can be calculated using the following formula:

$$L = \frac{1}{2\mathrm{Re}(k_{spw}^2 - k_s^2)^{1/2}} \tag{8}$$

3.2. **Surface plasmon resonance.** For nanoparticles, surface plasmon resonance is achieved when k_{sp} is equivalent to the wave vector of the incident light. To understand the phenomenon of SPR, consider the propagation constant of the electromagnetic wave in the metal along the metallic surface. For a metallic film, the electromagnetic field is defined by the complex wave vector given by

$$k_x = k_r + ik_{im} \tag{9}$$

The propagation constant to achieve surface plasmon resonance (k_{sp}) is given by

$$k_{sp} = \frac{\omega}{c}\left(\frac{\varepsilon_m \varepsilon}{\varepsilon_m + \varepsilon}\right)^{1/2} \tag{10}$$

where ε_m and ε are the dielectric constants and substantially larger than the imaginary component; the propagation constant can be estimated by

$$k_{sp} = \frac{\omega}{c}\left(\frac{\varepsilon_r \varepsilon}{\varepsilon_r + \varepsilon}\right)^{1/2} \tag{11}$$

Metallic nanoparticles differ from semiconductor quantum dots in many ways, including the means of modifying the optical spectra. While quantum dots require the quantization of electron and hole energy levels via quantum confinement in order to modify the optical spectra, metallic nanoparticles use light absorptive properties and the induction of surface plasmon resonance to modify the optical spectra. The absorption is the result of the collective oscillation of electrons induced by the interaction with the localized electromagnetic field; these oscillations produce surface plasmon waves. The sensor chip, which contained four sensing sites, was fabricated using MEMS technology. The chip material was polymer combined with glass chips, which deposited a layer of gold as the energy conveying layer, as shown in Figure 5.

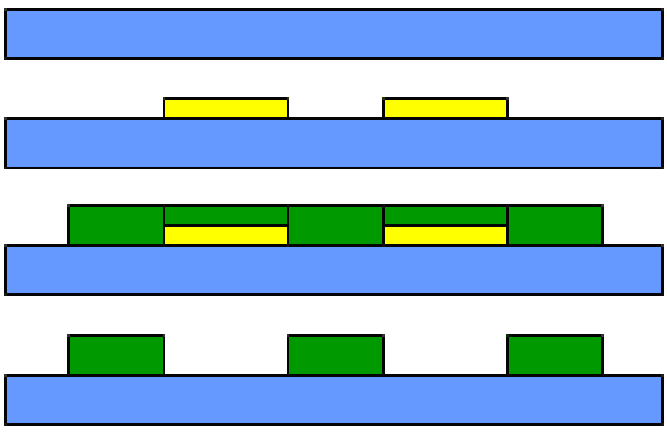

FIGURE 5. Fabrication process

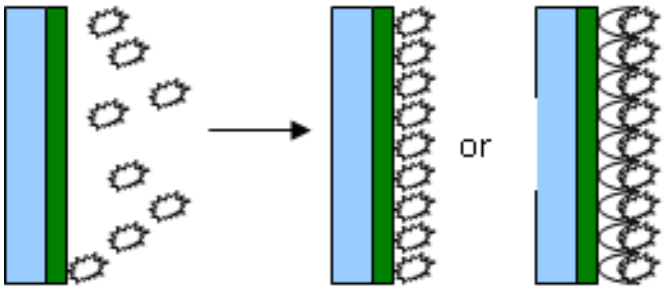

FIGURE 6. Absorption process

3.3. **Nanoparticles.** Although surface plasmon resonance can be achieved via energy transfer, as has been extensively described above, it can also be achieved by an electric field interaction. Recall that if an electric field is incident on a dielectric surface (E_0), the field within the material (E) is equivalent to the product of the dielectric constant (ε) of the material and the incident electric field. Note that the dielectric constants of a non-absorbing material and its corresponding refractive index, n, are related. Gold nanoparticles can be fabricated under solution condition, and the optical scattering effect comes from surface plasmon resonance. The optical property is influenced by the wavelength of the incident light and the particle sizes. In this research, the nanoparticles were fabricated by gold tri-chloride and a reducing agent, and were 10 to 100 nm in size.

The nanoparticles absorbed onto the sensor chip by the electric field driving method, which allowed for the precise control of the quality and quantity of the surface particle layers, as shown in Figure 6.

4. **Gold Nanoparticle Characterization and Analysis.** We revisit now our modeling of the gold films for SPR to include this surface roughness. The modeling of discrete metal films has attracted the interest of physicists for the past century. Similar tests were performed on samples of synthesized gold nanoparticles. This data provided information as to the baseline absorption for 20 nm gold nanoparticles. Prior documentation noted that the maximum absorption for 2-5 nm gold nanoparticles was observed at 517 nm; however, a comparison of a known sample of 20 nm gold nanoparticles with our synthesized particles indicated that the absorption peak for 20 nm gold nanoparticles was in the range of 521-530 nm. We should note that fluorescence data was not collected on gold-only or silver-only samples since the data consisted, primarily, of scattered pump wavelengths. The synthesized 20 nm gold nanoparticles were wine red in color, corresponding to Mie's theory of gold nanoparticles noted earlier in this document. Based on the solution color and the absorption data, the particle size was verified. Figures 7 and 8 give the comparison of a known sample of 20 nm nanoparticles with the synthesized nanoparticles we generated. TEM images, not shown, of the two samples were also used for size verification. As shown in Figure 8, the absorption peaks were at 550 nm and 588 nm. This indicated that maximum absorption occurred at these wavelengths. This data coincided with both the PLE and the PL data collected previously.

5. **SPR Analytical Applications.** The phenomenon of SPR is completely non-specific, in that it cannot distinguish between different chemical changes. While this may appear to be a limitation, it is really a powerful advantage. Specificity depends upon the selection of pairs of molecules which react only with each other. One member of the pair is the detector and the other is the target analytic (i.e., the substance we wish to detect/quantitate) [16]. Any pair of molecules which exhibit specific binding can be adapted to SPR measurement.

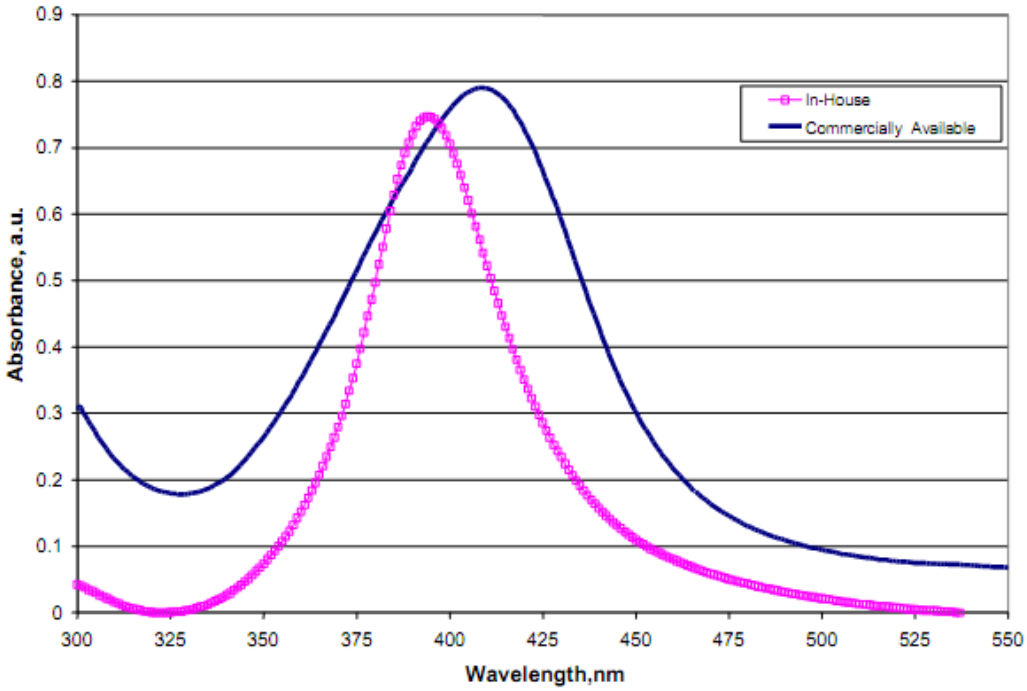

FIGURE 7. Absorption comparison of known-sized gold nanoparticles and the generated sample

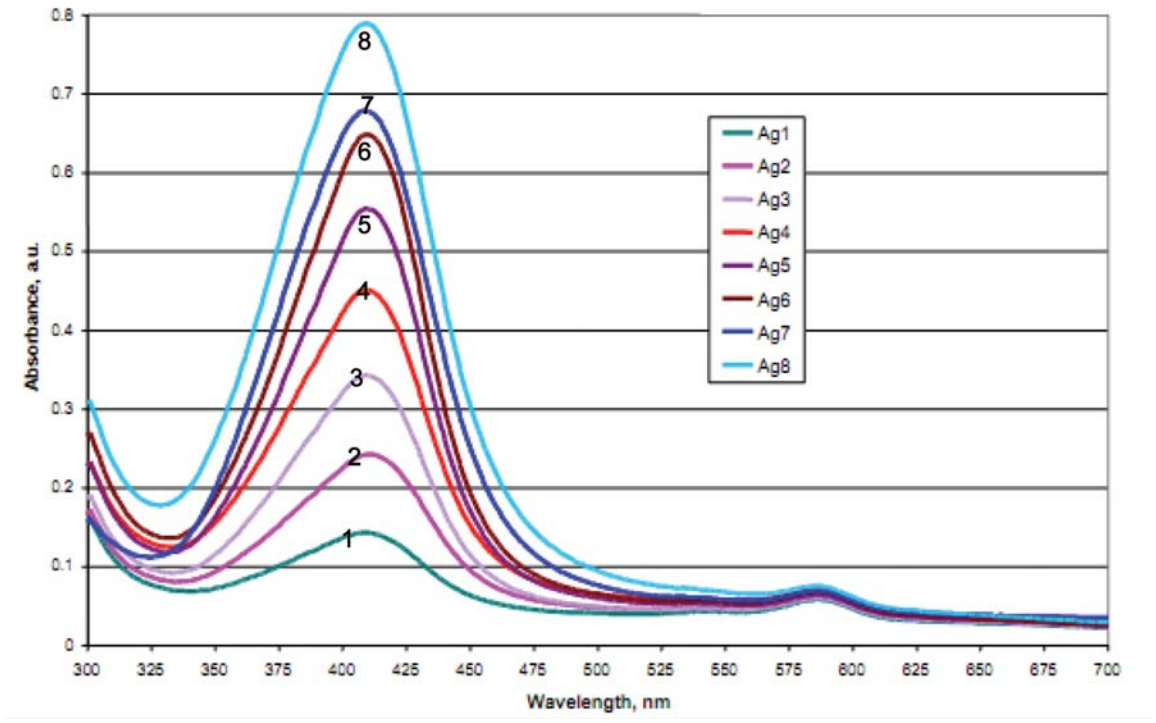

FIGURE 8. Absorption data obtained for diluted S101 sample

These may be an antigen and antibody, a DNA probe and complementary DNA strand, an enzyme and its substrate, oil, gas or liquid, which is soluble in the oil, or a chelating agent and metal ion as shown in Figure 9.

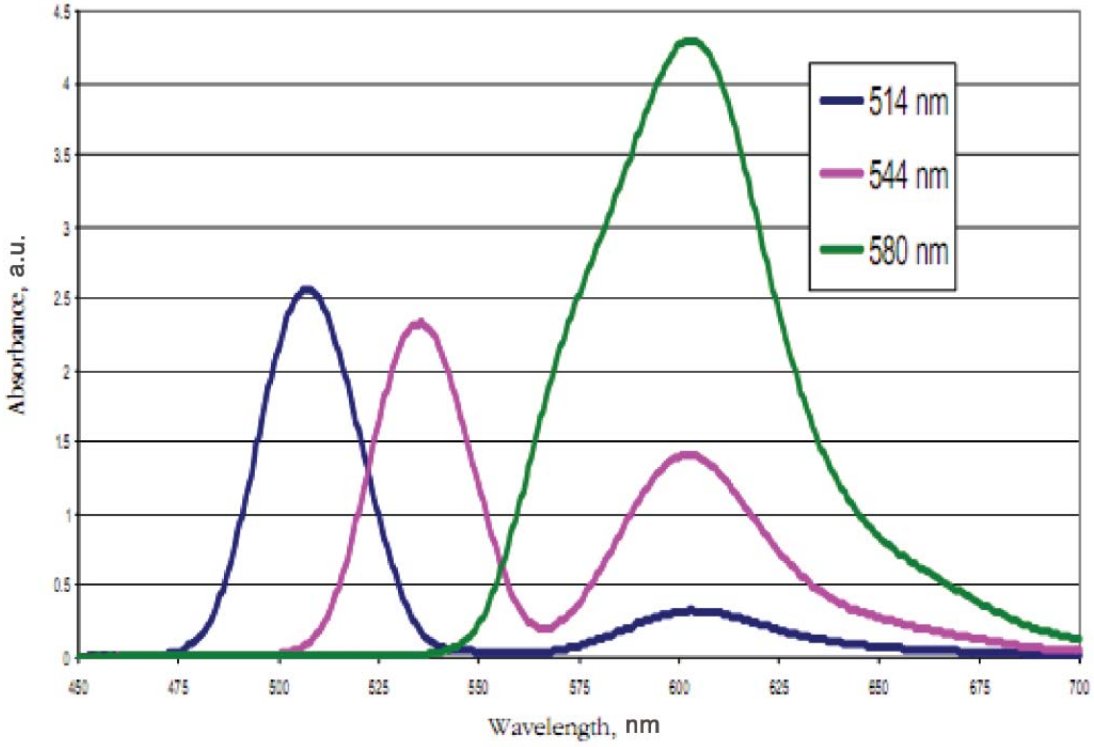

FIGURE 9. Characterization of the gold surface roughness

SPR can be used as the basis for a sensor which is capable of sensitive and quantitative measurement of a broad spectrum of chemical and biological entities. It offers a number of important practical advantages over current analytical techniques. The time from sample application to reported result varies with the specific chemistry, but it can be as short as 5 min. In most cases there is no need to pretreat the sample before its presentation to the sensor. A single sensor format (i.e., size, storage and usage protocol, reader) may be used for a variety of assay chemistries, including immunological, nucleic acid binding, enzymatic, chemical and gas adsorption.

6. **Conclusion.** This paper will discuss the whole system, which contains microsensor, preamplifier and signal processing circuit. This report continues on previous effort in spirometric MEMS sensor, for bi-directional flow. Surface plasmon sensors have been used to probe large areas, and the heterogeneity of the gold film was probably not a critical parameter. Although the first attempts of surface plasmon imaging date back more than ten years [18], its application to biochips is still emerging. It is, therefore, very important that the users of plasmon chips be aware of the sensitivity of the surface plasmon microscopy, not only as to the thickness of the gold films, but also as to their bulk heterogeneity. The results described in Chapter 3 have provided a progressive step in understanding the behavior of silver and gold nanoparticles in a fluorescence dye (fluorophore) system. We have noted several theories about the excitation of surface plasmons in Chapters 1 and 2 and have described the reaction to these excitation mechanisms. Building on the principle theory of light scattering (Rayleigh scattering), Mie described a system that considered the affects of the surrounding media with the incident light and how its response affected the response of the excited molecule. Raman further exploited this theory by observing the change in frequency of the exiting radiation from the sample. Finally, Förster and Dexter combined these theories to describe the energy transfer

from the excited donor to the acceptor. Our system, described extensively, has displayed properties of all of these theories of excitation.

During the last 20 years the surface plasmon resonance technique has been developed into a very useful technology with numerous applications. In order to illustrate the potential of SPR sensing devices, the major application areas of SPR sensors have been outlined. This research combined the optical, chemical, electrical and biomedical fields, which was a challenging task. This paper described the method to monitor nanoparticle and biomedical materials, which have an enormous potential in clinical uses. The portable biochemistry analyzer will be discovered through a similar detection method.

We began our research with the intent of developing an optical sensor that optimized surface plasmon resonance to amplify a signal within the sensor. We soon discovered that understanding the interactions between the nanoparticles and the dye was significant before incorporating it into a system with a variety of other components. We chose a dye, similar in characteristics to the dye we wished to use in the sensor, to study the effects. After noting that previous research used thin films, we decided to investigate the colloidal system instead, since the final system combined the nanoparticles in the sensor itself.

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