Fabry-Perot type sensor with surface plasmon resonance

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The main point of this letter concerns the fabrication of an optical sensor with improved sensitivity for detecting molecular adsorption onto a gold surface. The sensor consists of a Fabry-Perot interferometer whose one of two reflective layers is constituted by an island-type gold film having a pronounced local surface plasmon resonance. The results presented in the letter show that the binding of molecules on the device surface induces a differential interference pattern whose amplitude is increased by the plasmon resonance. The sensor sensitivity can be improved by further deposition of Au nanoparticles on the reflective layer. This kind of sensor has potential advantages since it is easy to fabricate and use and it possesses a submonolayer sensitivity. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2398885]

The Fabry-Perot interference phenomena have been used to develop various sensors for temperature, strain, pressure, and biomolecules because of their high sensitivity and accuracy. Typical application schemes are fiber-optic cavity sensors to detect the molecules deposited on the fiber end[1] and fiber Bragg grating sensors which show a very high sensitivity to the refractive index of the contacting medium.[2] Recently, an interesting study has shown that electrochemical etches of single crystal *p*-type Si wafers can produce porous materials that display well-resolved Fabry-Perot fringes in their reflectometric interference spectrum. Such materials can be used as sensors since the Fabry-Perot fringe pattern undergoes significant wavelength shifts upon molecule binding.[3–5] As we know, light can interfere after reflection on the two interfaces of a thin transparent membrane as, for example, a soap bubble. Such interferences were widely studied in the case of parallel-faced dielectric film: for instance, the reflectometric interference spectroscopy (RIFS) device developed by Gauglitz and co-workers is a simple and sensitive label-free detection method.[6,7] Commonly, this RIFS transducer chip consists of a SiO_2 layer sandwiched between a high refraction Nb_2O_5 layer and a sensitive layer such as antigen, antibody, or biopolymer.

However, few reports can be found for the use of ultrathin noble metal film as the sensitive layer in this type of device despite numerous expectable advantages: not only the helpful Au–S bond but also a sensitive response to molecule binding. Indeed, under a severe control of evaporation parameters,[8,9] nanostructured thin Au films can exhibit a local surface plasmon resonance (SPR) peak that depends on the island morphology and whose position is sensitive to the dielectric properties of the contacting medium.[10] Transmis-

sion surface plasmon resonance spectroscopy is widely developed to detect the binding of various analytes, such as small molecules, proteins, and DNA hybridization.[11–13] Here, we present then a simple fabrication method of an optical sensor which combines both the surface plasmon resonance of ultrathin gold films and the effects of Fabry-Perot interferences with the expectation of making a highly sensitive optical sensor.

The Fabry-Perot interferometer proposed consists of a $BaTiO_3$ layer with a thickness of about 2.5 μm sandwiched between two thinner reflective layers, one of silver with a thickness of 80 nm and the other of nanostructured gold with a thickness of 6 nm (Scheme 1). Each layer was deposited successively onto a transparent quartz substrate using a pulsed laser deposition (PLD) technique carefully described in a previous report.[14] Silver was chosen for its good optical reflective properties. It was deposited at room temperature,
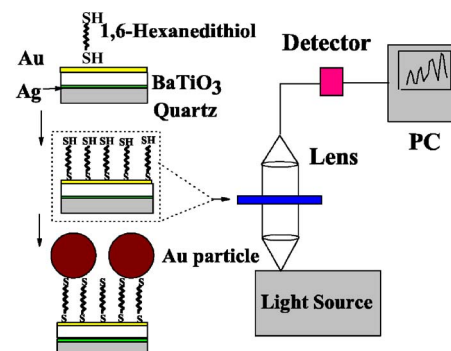
SCHEME 1. Design and experimental setup for the Fabry-Perot SPR sensor. Silver, $BaTiO_3$, and islandlike gold layers are deposited by PLD on a quartz substrate to compose the Fabry-Perot sensor. Then, 1,6-hexanedithiol is introduced onto the gold surface, and gold nanoparticles are eventually immobilized. Transmission UV-vis spectroscopy is used to monitor the optical properties of Fabry-Perot type films.

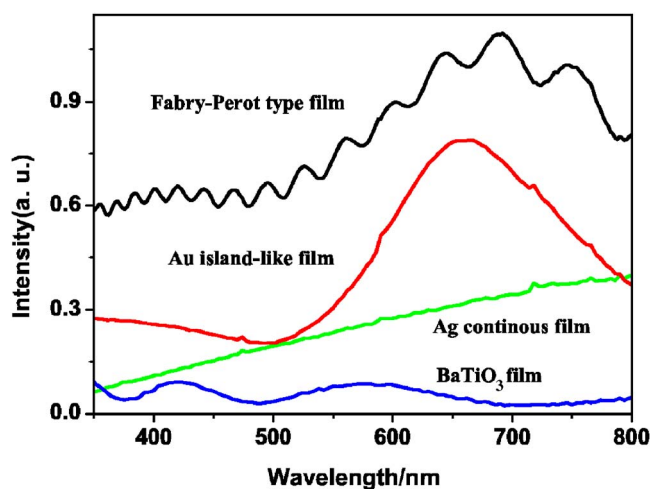[a]Deceased.
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FIG. 1. Transmission UV-vis spectroscopy for a 2.5-μm-thick BaTiO$_3$ thin film, a 80-nm-thick silver film, and a 6-nm-thick gold film deposited on a quartz substrate at 25, 25, and 200 °C, respectively, and for the entire Fabry-Perot type film described in Scheme 1. All measurements were collected in air.

which ensures that the film is flat with a roughness measured by atomic force microscopy of less than 0.3 nm and possesses the simple shape of an extinction spectrum characteristic of bulk sample[15] (here roughness is defined as the standard deviation of the height value within a bow cursor with a size of 250×250 nm^2 and a resolution of 256×256). BaTiO$_3$ was chosen because it is transparent in the visible range and stable in aqueous solution. It was deposited at room temperature, which allows again to mimic the roughness.[16] Finally, aiming to investigate whether the surface plasmon can induce a strong modification of the Fabry-Perot fringes upon species adsorption, an islandlike gold film was chosen as the external sensitive layer. It was obtained by PLD technique at 200 °C substrate temperature, which was already proved to induce a strong corrugation characterized by a large roughness of around 2 nm.[17] The absorbance spectra are obtained by a commercial UV-vis absorbance instrument in transmittance model. Figure 1 shows the individual absorption of each layer of the sensor (measured after deposition on glass of each layer alone) and that of the entire sensor itself. The results clearly show that for the sensor so elaborated (1) Fabry-Perot interference fringe patterns are effectively obtained and (2) the amplitude of the fringes is strongly increased around the plasmon resonance peak. Generally, sensors consist of a highly specific recognition element and a transducer that converts the molecular recognition event. Here, the nanostructured Au thin film both "recognizes" organic molecules via Au–S covalent binding and fulfills an important transducer role via SPR.

The interference sensor device so elaborated is used as an optical sensor to detect the adsorption of molecules onto a gold surface. The sensor was fixed in a flow cell. Then the cell was mounted on the sample stage of the absorbance instrument. After treating with the analyte solution, the sensor was washed several times with ethanol and finally dried under nitrogen flow. Before molecular adsorption, we verify the reliability of the sensor by measuring several times the extinction spectrum of the sensor in the same conditions. A typical result is given in Fig. 2(a). The spectrum does not undergo any obvious variation and the difference spectrum shown in the bottom of Fig. 2(a) has a small random signal.
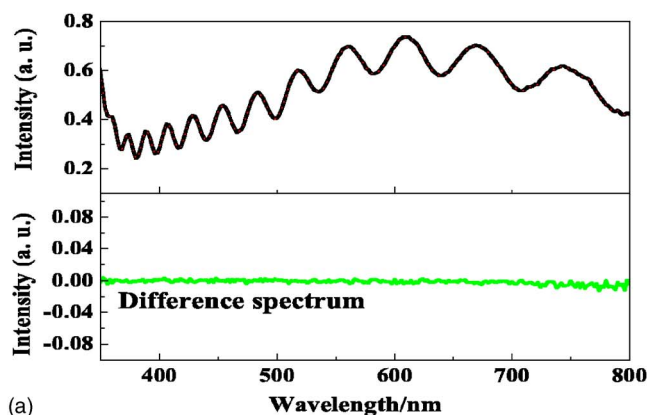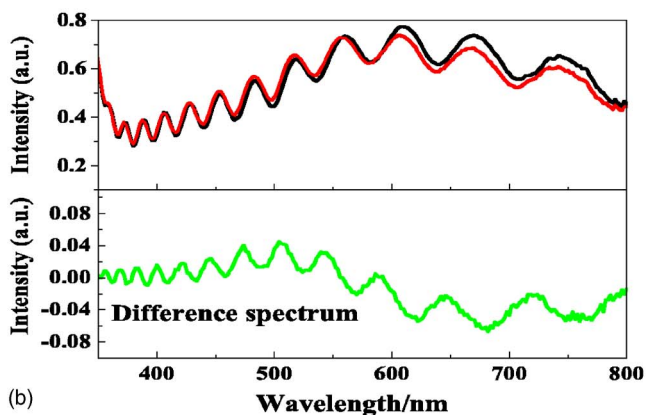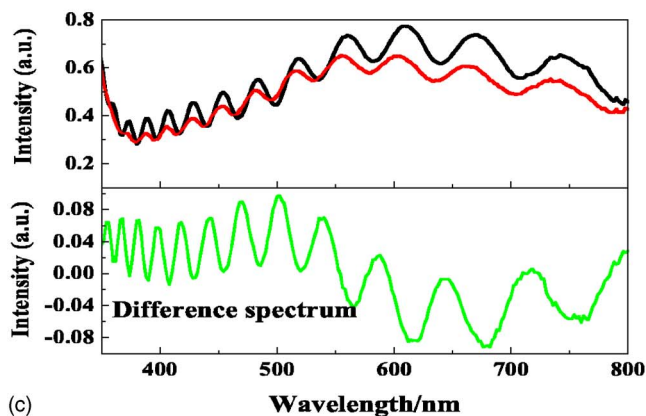
FIG. 2. Black spectrum is a reference fringe pattern of the untreated sensor. The red spectra refer to the untreated sensor (a), treated with 1,6-hexanedithiol (b), and gold particles (c). In each case, the green spectra are the difference between the black and red interference spectra. All measurements were collected in air environment with unpolarized light and about 1 mm probe diameter. A home-built cell was used to measure the spectrum *in situ*.

This indicates that the system has a good reliability. Then, the interferometer device was immersed in 5 mM 1,6-hexanedithiol ethanol solution for different durations, and the spectra were measured. Typical data are shown in Fig. 2(b) when the device was immersed in the solution for 4 h. After immersion, the spectrum undergoes a small blueshift and a slight shape change, and the difference spectrum between the treated and untreated sensors presents now a clear interference fringe pattern. The blueshift, shape variation, and spectrum difference of the spectrum mount up when the immersing time increases. Furthermore, Au nanoparticles were used to enhance the signal. Precisely, gold colloids with a diameter of about 13 nm, synthesized using the Frens method,[10,18]

were also injected into the cell after a previous treatment of the sensor in 1,6-hexanedithiol for 4 h. Au particles were maintained in contact the sensor for 4 h before the cell was flushed with ethanol and dried under nitrogen. The results, shown in Fig. 2(c), display an obvious modification in the patterns resulting in further spectrum blue shift and larger difference spectrum signal. To demonstrate that the Fabry-Perot sensor presented here is more sensitive than a simpler Au thin film, this device was compared to a 6-nm-thick Au film deposited alone on a glass substrate (at 200 °C). Both were treated with 1,6-hexanedithiol ethanol solution for 60 s in the same conditions. The results show that the SPR of the ultrathin Au film does not present any noticeable peak shift, whereas the interferometer device shows a smaller but clear difference spectrum (data not shown here). This demonstrates that ultrathin Au films with SPR properties present better sensitivity when they are integrated in a Fabry-Perot device. A probable reason should be that the absorbance spectrum of Au films is mostly sensitive to the k part of the optical constant, while the spectrum difference of the Fabry-Perot fringes depends on both the k and n parts of this constant. However, more detailed studies are clearly needed to determine the exact mechanisms as well as the detection limit of this sensor.

Ideally, optical thickness and surface reflectivity are two main factors which determine the interference pattern in standard Fabry-Perot interference devices. The optical thickness which determines the position of the interference spectra is the product of the physical thickness and the refractive index of the sensitive layer. From the experimental results shown, the change in the effective optical thickness generated by molecular adsorption can be quantified. It is about 24 nm (from 6436 to 6412 nm) for the blueshift shown in Fig. 2(b). The adsorption of Au nanoparticles, which induces a further blueshift, leads to a greater optical thickness change of about 64 nm [from 6436 to 6372 nm according to Fig. 2(c)]. Moreover, the intensity of the interference pattern at long wavelength (>600 nm) gradually decreases after molecular adsorption, while it does not present any significant variations at short wavelength. When Au nanoparticles are introduced, the intensity of the interference pattern undergoes a further and strong decrease at long wavelength and the oscillation amplitude of the interference pattern (related to the resolvance of the interferometer) decreases obviously. The first reason is that the adsorption of Au particles on the sensor can induce a redshift[19–21] of the broad SPR band of the films. Since this band is located at around 700 nm, this could cause a drastic change in the fringes at long wavelength.[21,22] The second reason is that the Au particles could induce a change in the Au layer surface fidelity, an increase of light scattering by gold particles, or a decrease in the surface reflectivity.

It should be emphasized that the BaTiO$_3$ layer of the interference sensor could be replaced by SiO$_2$ layer without changing the sensor mechanism, i.e., the optical sensor could also be fabricated simply by thermal evaporation technique. Moreover, the sensitive layer of the sensor, i.e., the nano-

structured Au surface, could also be replaced by nanoparticle arrays synthesized using nanosphere lithography[12] or subwavelength holes,[23,24] which should provide other interesting schemes for the sensitive sensor presented in this letter.

In conclusion, a sensitive optical sensor combining the Fabry-Perot interference and Au SPR effects was fabricated and applied to detect molecule adsorption onto a Au surface. The molecular adsorption onto the sensor results in a spectrum blueshift and a spectrum shape variation, which can be amplified by further adsorption of Au nanoparticle. The sensor can be fabricated easily with PLD or thermal evaporation technique and applied by using commercial UV-vis spectrometers. Tests on biological molecules are now in progress.

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