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Ultrasensitive sensors using enhanced surface plasmon resonances in capped metallic nanostructures

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Abstract

Nanostructure-based sensors are capable of label-free detection for sensing applications. However, plasmonic sensors capable of highly sensitive detection are desirable. We show that capped metallic nanostructure arrays made by thermal-embossing nanoimprint method on a polymer film can produce extremely sharp asymmetric resonance for transverse magnetic-polarized wave. An ultrasmall linewidth is formed due to Fano coupling between cavity resonance mode in nanoslits and surface plasmon resonance mode on periodic metallic surface. The full width at half-maximum bandwidth of the Fano mode is 3.68 nm. The wavelength sensitivity is 900 nm/RIU. The highest figure of merit is up to ~250. The obtained value is much higher than the prism-coupling SPR sensors and the previously reported values in other nanostructure-based sensors.

1. Introduction

Surface plasmon resonance (SPR) sensing is a real-time and label-free detection technique which has been employed in applications including medical diagnostics, environmental monitoring, and food safety. The most common method to induce SPR on the gold surface is to utilize an optical prism, known as the Kretschmann configuration. On the basis of this SPR excitation technique, commercial instruments enable real-time and label-free measurements of biomolecular binding affinity. In addition to the prism coupling method, metallic nanostructures offer a simple way for SPR excitation. Recently, periodic gold nanohole arrays or nanoslit arrays have been utilized for biosensing applications. Compared to prism-based SPR sensors, gold nanostructures benefit from having a small detection volume and normal light incidence. They provide a feasible way to achieve chip-based, high-throughput and label-free detection for modern DNA and protein microarrays.

In order to reach the best sensing performance, sensors having ultrahigh quality factors are required. Narrower resonance linewidth allows a lower molecular concentration to be detected. The linewidth is related to the surface plasmon propagation loss. An approach to achieve sharp spectral response is based on Fano resonances.[1] The Fano resonance exhibits a distinctly asymmetric shape which arises from the interference between spectrally overlapping a broad resonance and a narrow discrete resonance. The Fano resonances have been extensively studied in nanoparticles, plasmonic nanostructures and metamaterial systems. In this paper, we show that a transverse magnetic-polarized wave in the capped gold or silver periodic nanostructures can generate extremely sharp and asymmetric Fano resonances in transmission spectra. The full width at half-maximum bandwidth (FWHM) was only 3.68 nm and the wavelength sensitivity was 900 nm/RIU, based on the period in the nanostructures. The extremely sharp resonance leads to an ultrahigh intensity sensitivity up to 48117 %/RIU. Compared to previous single-layer SPR sensors, the proposed structure has a much narrower bandwidth. It reaches a figure of merit (FOM) up to 250. We attribute such high sensitivity to enhanced resonant effects by the gold capping layer. It caps the gap plasmon in nanostructures, resulting in an enhanced cavity mode. In addition, the surface plasmon wave between the periodic-metallic surface has a better confinement, resulting in an enhanced SPR mode. The strength of Fano coupling between these two modes can be tuned by the thickness of gold film and nano-apertures. An optimal Fano coupling is achieved when the capping layer is close to the height of the nanostructures.

2. Fabrication of the chip

Nanostructure arrays were madd by using a thermal-embossing nanoimprint method.[2] First, a silicon mold was fabricated using electron beam lithography and a reactive ion etching method. A 300-nm-thick resist was spin-coated on a silicon substrate. An electron-beam drawing system was used to write nanostructure arrays with various widths. The patterns were then transferred to the silicon substrate by using a reactive ion etching machine. The patterned silicon template and plastic substrate was placed on a heating plate. It was heated at a temperature of 170^{o}C to soften the plastic substrate. A uniform pressure (2 kgw/cm^2) was acted on the film. The template and plastic substrate were then cooled and taken out from the chamber. A 80-nm-thick gold film was then deposited on the plastic film using an electron gun evaporator. Fig. 1 depicts a process flowchart for the fabrication of metallic nanostructures and the SEM image of the silicon mold and gold coated nanostructures on a plastic film.

3. Transmission spectrum measurement

The transmission spectra were measured by a simple optical transmission setup. A white light was focused on a single array. Its incident polarization was controlled by a linear polarizer. The transmission spectrum was taken by using a fiber-coupled spectrometer. Fig. 2 shows the measured and calculated Fano resonance spectra of capped nanoslit arrays with different periods. The resonant wavelength is determined by the period.

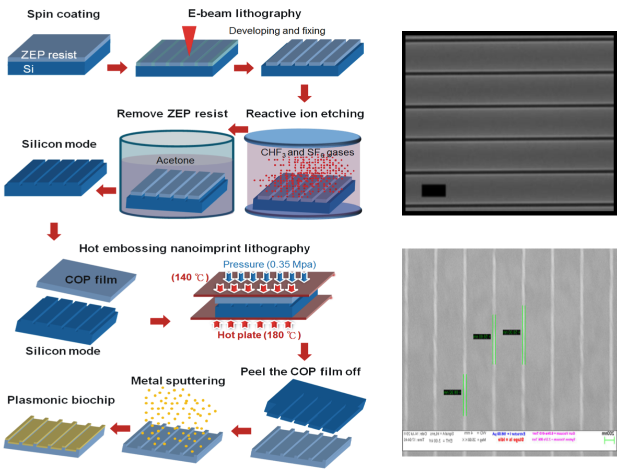
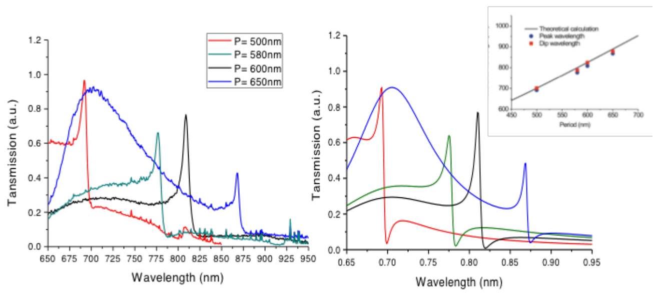


Fig. 1 (left)The fabrication procedures of nanostructures. (right) The SEM images of the Si mold and imprinted capped nanoslits.



(a) (b)

Fig. 2 (a) The measured and (b) calculated Fano resonant spectra for different gold nanoslit arrays. The inset shows the resonant wavelength as a function of period.

To verify the high sensitivity of the capped gold nanostructures, we tested the refractive index sensitivity of the nanostructure with a period of 650 nm. The bulk sensitivity of the sensor was measured by injecting purified water mixed with various ratios of glycerin into the microfluidic devices. Fig. 3a shows the intensity spectra of the capped gold nanoslits with various water/glycerin mixtures for a normally-incident TM-polarized wave. There were sharp Fano resonances in the spectra. The wavelength of the Fano resonance at the water/gold interface is near 870 nm. When the concentrations of glycerin increased, the wavelength of Fano resonance was redshifted and the intensity changed. Fig. 3b shows the resonant peak wavelength and intensity against the refractive index of the outside medium. The measured fwhm bandwidth of the Fano resonant peak were 3.68 nm. As the wavelength sensitivity is proportional to the period, the wavelength sensitivity will be close to 900 nm/RIU. Thus, the estimated FOM value will be up to 250. Fig. 3c shows the normalized intensity change against the refractive index of the outside medium. The slope of the fitting curve shows that the intensity sensitivity is 48117 %/RIU. The measured intensity sensitivity is much better than the reported intensity sensitivities of nanoslit, nanohole or nanogrid arrays and prism-based SPR sensors. The current structure can achieve a detection limit of 4.15×10^{-6} RIU when the intensity resolution is 0.2%. Such a detection resolution is comparable with commercial SPR machines using complicated high-resolution angular detection method. To verify the applications for biosensors, the interactions between bovine serum albumin (BSA) and anti-BSA were measured using capped gold nanoslits with a 600 nm period. Fig 3d shows the measured spectra for different surface conditions. Significant changes in wavelength shift were observed when BSA and anti-BSA were bound on the gold surface. The monolayer BSA results in a 0.40-nm red shift. The wavelength shift is small because BSA is a small molecule with 66 kDa in size. The wavelength shift for anti-BSA molecules is large. The 150-kDa-sized anti-BSA resulted in a 2.76-nm wavelength shift.

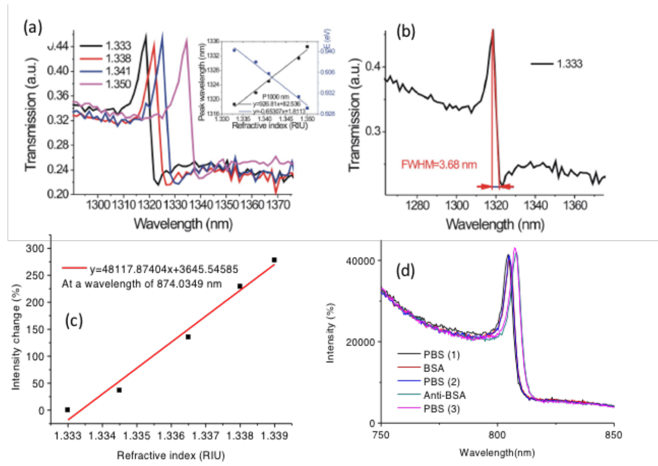


Fig. 3 (a) Transmission spectra at different medium. (b) the bandwidth of the Fano spectrum. (c) The intensity sensitivity of the Fano sensor. (d) The resonant spectra at different protein coatings.

4. Conclusions

The experimental results show that a transverse magnetic-polarized wave in the capped gold nanostructures generated extremely sharp and asymmetric Fano resonances in transmission spectra. It reaches a record FOM up to ~ 250. The proposed structure with highly sensitive Fano resonances can be applied to develop colorimetric test strips for point-of-care applications. Such inexpensive, reproducible and high-throughput fabrication of highly sensitive capped nanoslits can benefit sensing applications.

Acknowledgements

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References

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