High-sensitivity surface plasmon resonance spectroscopy based on a metal nanoslit array

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We have chemically modified metal nanoslit array surfaces with alkanethiol self-assembled monolayers and have characterized the resulting spectral shift of optical transmission. Adsorption of a self-assembled monolayer (1.5 nm thick) on a silver nanoslit array (slit width of 30–50 nm and grating period of 360 nm) is found to cause an 11 nm redshift of the main transmission peak. Strong confinement of optical fields in the narrow slit region allows sensitive transduction of surface modification into a shift of surface plasmon resonance wavelength. © 2006 American Institute of Physics. [DOI: 10.1063/1.2209717]

Surface plasmon resonance (SPR) spectroscopy is widely used in chemical and biological sensing.\(^1\) The SPR technique senses the integral changes in the dielectric ambient in the vicinity of the metal surface that supports the surface plasmon waves.\(^2\) At a planar metal/dielectric interface, the plasmon fields evanescently extend into the dielectric with 200–300 nm depth and into the metal with 20–30 nm depth.\(^3\) In the case of metal particles or thin metal island films, the plasmonic fields can be more narrowly confined to the metal surface with 10–30 nm penetration depth to adjacent dielectric.\(^4\) Strong confinement of plasmonic fields near the metal surface can be utilized for the benefit of enhancing plasmonic interactions with an analyte layer and thus for efficient transduction and sensing of surface binding events. Recently there has been a growing interest in SPR sensing of biochemicals using a nanostructured metal layer, such as nanoparticle or nanohole arrays.\(^4\)–\(^8\)

In this letter we report a transmission SPR sensor based on a metal nanoslit array structure. A metal nanoslit supports guided modes without cutoff wavelength, whereas optical transmission through a metal nanohole array is critically limited by the hole size and metal thickness.\(^9\)–\(^12\) This feature suggests that metal nanoslit arrays may be intrinsically more suitable for transmission-mode SPR sensing.

Figure 1 (inset) shows a schematic drawing of the silver nanoslit array structure studied in this work. A 190-nm-thick Ag slit array was formed on a quartz substrate. The slit width is designed to be in the range of 30–50 nm, and the grating period is 360 nm. Details of fabrication of the Ag nanoslit array structure have been described elsewhere.\(^12\) The sample was then chemically treated to coat the metal surface with an alkanethiol self-assembled monolayer (SAM) [HS(CH\(_2\))\(_7\)-COOH]. Alkanethiols form dense, well-ordered, tightly bonded films on Ag, and the SAM can be easily tailored to incorporate a variety of molecular recognition elements designed for specific binding.\(^13\) Optical transmission through the Ag nanoslit array was then characterized in the spectral range of 350–1750 nm, using unpolarized light at normal incidence. The as-deposited nanoslit array shows a characteristic transmission spectrum with clear peaks defined by transmission minima (the black curve in Fig. 1). Light which is incident on the nanoslit array excites surface plasmons (SPs) on the nanoapertured metal surface, and the SP waves are funneled into and propagate through each slit. Part of the SPs emerging from the slits couples into the SP waves propagating laterally towards the neighboring slits, while some decouples into radiation modes. The laterally propagating SPs encounter a periodic perturbation introduced by the slit array and form Bloch waves. The SPs’ periodic interaction with the media results in formation of plasmonic band gap around the resonance point, similar to the dielectric-based photonic crystal’s case.\(^14\)–\(^15\)

Adsorption of a SAM causes a redshift of the transmission spectrum (the red curve in Fig. 1). The amount of redshift measured with the main transmission peak at around 690 nm is 11 nm. The thickness of the SAM is estimated to be 1.5 nm. The sensitivity of this response, defined as the ratio of the transmission spectral shift to the adsorbed analyte layer thickness, is calculated to be 7. In the case of nanohole-array-based SPR sensing, a sensitivity of 2.5 was reported: 4 nm spectral shift for adsorption of a 1.7-nm-thick SAM on Ag nanoholes, measured with similar analyte/ambient dielec-

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FIG. 1. (Color online) Optical transmission through a Ag nanoslit array: before chemical modification of metal surface (black) and after adsorption of an alkanethiol self-assembled monolayer (red). The inset shows a schematic drawing of the fabricated Ag nanoslit array structure (after adsorption of a SAM).
tric contrast, i.e., \( \varepsilon_a / \varepsilon_d = 2.1 / 1.0. \) In order to better understand this nanoslit-array-based SPR sensor’s response to analyte coverage, we have analyzed the plasmonic interaction of an incident light wave with an adsorbed analyte layer.

Figure 2 shows the finite-difference time-domain (FDTD) analysis of the SP polarization charge distribution on a metal surface calculated at 650 nm wavelength, which is close to the peak transmission point. The polarization charges show a quadrupolar distribution along the periphery of each metal island separated by slits. A single period of charge oscillation spans one plasmonic wavelength, and the plasmon wavelength depends on the nature of metal/dielectric interface. From the quadrupolar resonance condition, the optical wavelength at the transmission peak can be expressed as follows:

\[
\lambda = (1/2)L_1 \text{Re}(n_{e1}) + (1/2)L_2 \text{Re}(n_{e2}) + L_3 \text{Re}(n_{e3}).
\]  

(1)

Here \( L_1 \) is the length of the top surface section (air side) of a metal island, \( L_2 \) the length of the bottom surface (substrate side), and \( L_3 \) the height of metal sidewalls, i.e., slit depth. \( n_{ei} \) (\( i = 1,2,3 \)) is defined as the SP wave vector normalized by the free-space propagation constant \( k_0 \) and corresponds to the effective index of the metal/dielectric interface being considered. The effective index \( n_e \) is, in general, a complex number, having both propagation and attenuation components. In the case of Ag, SP wave vectors are propagation dominant in the visible to near-infrared range. In this work with a submicron-period slit array, therefore, we neglect the imaginary part of the effective indices. Along the transverse direction, the SP fields evanescently extend into both metal and dielectric regions. The effective index value reflects the integral effects resulting from interactions of a plasmon wave with the media over the entire extension of the fields. Chemical modification of each metal surface is expected to alter the effective index \( n_{ei} \) in that section, by an amount commensurate with the change in the plasmonic fields in the dielectric ambient, causing a resonant wavelength shift. The dispersion property of materials (especially the wavelength dependence of metal’s dielectric function) in conjunction with a spectral shift also contributes to the effective index change. Taking into account these two contributing factors we can express the total wavelength shift as follows:

\[
\Delta \lambda = (1/2)L_1(dn_{e1}/d\lambda)\Delta \varepsilon_d + L_2(dn_{e2}/d\lambda)\Delta \varepsilon_d + L_3(dn_{e3}/d\lambda)\Delta \varepsilon_d / \left[ 1 - (1/2)L_1(dn_{e1}/d\lambda) - L_2(dn_{e2}/d\lambda) - L_3(dn_{e3}/d\lambda) \right].
\]  

(2)

The effective index changes caused by chemical modification are expected to be different for the top surface of a metal island and the slit sidewalls. Hence they will show different sensitivities to an adsorbed analyte layer, because of the different distribution of plasmonic fields along the transverse direction. To find the effective index change for the top surface section, we model it as a planar metal/dielectric interface with semi-infinite extension of dielectric. The effective index for SPs on that surface can be expressed as \( n_{ei} = \text{Re}(\varepsilon_m \varepsilon_a)/(\varepsilon_m + \varepsilon_a) \), and the dispersion term \( (dn_{e1}/d\lambda) \) is determined as \( (1/2)n_{e1}\varepsilon_m^{-1/2}(d\varepsilon_m/d\lambda) \). Imagine that an analyte layer of thickness \( d \) and dielectric constant \( \varepsilon_a \) is adsorbed on the metal surface. Assume that the analyte layer thickness is much smaller than the plasmon field extension (i.e., the penetration depth in dielectric). The SP effective index change caused by analyte adsorption \( (dn_{e1}/d\lambda)\Delta \varepsilon_d \) can be expressed as follows:

\[
\frac{dn_{e1}}{d\varepsilon_d} \Delta \varepsilon_d = \frac{\pi}{\lambda} \frac{\varepsilon_m^{3/2}\varepsilon_d^{1/2}}{(\varepsilon_m + \varepsilon_a)^2} \left( 1 - \frac{\varepsilon_d}{\varepsilon_a} \right) d.
\]  

(3)

The index change in the slit requires more development. In the case of a metal slit of width \( w \), propagation of a plasmon wave along the slit is governed by the following dispersion relation:

\[
\gamma_m + \gamma_d \frac{1 - e^{-\gamma_d w}}{e^{-\gamma_d w} + 1} = 0.
\]  

(4)

Here, \( \gamma_d = (k_{SP}^2 - \varepsilon_m k_0^2)^{1/2} = k_0(n_{\varepsilon_d}^2 - \varepsilon_d)^{1/2} \) is the decay constant of plasmon fields inside the slit region and describes the evanescent profile in the dielectric gap. The decay constant in the metal region, given by \( \gamma_m = (k_{SP}^2 - \varepsilon_m k_0^2)^{1/2} = k_0(n_{\varepsilon_m}^2 - \varepsilon_m)^{1/2} \), determines the penetration depth in metal. Figure 3(a) shows the effective index \( n_{e3} \) (both the real and imaginary parts) calculated for a silver nanoslit with air gap by solving the dispersion relation at three different wavelengths, 450, 650, and 800 nm. As assumed before, the imaginary part remains small compared to the real part so that SP attenuation would be insignificant for the slit dimensions being considered. The effective index monotonically increases as the slit width decreases. For the case of a 40 nm slit width, the effective index is calculated to be 1.5 at 650 nm. Figure
3(b) shows the $E_x$ field distribution (the $E$-field component normal to metal surface) calculated for the same slit structure. The field remains nearly constant across the gap region, whereas it quickly decays in the metal with a penetration depth of ~30 nm. By differentiation of Eq. (4) with respect to $\lambda$, we obtain an expression for \( \frac{dn_{y3}}{dE_0} \). The effective index change induced by analyte adsorption can be expressed as \( \frac{dn_{y3}}{dE_0} \Delta n_{y3} \). $\Delta n_{y3}$ represents the change of dielectric ambient in the slit region caused by adsorption of analytes on slit walls. For the case of analytes of dielectric constant $\varepsilon_a$ and thickness $d$ on each sidewall, \( \Delta n_{y3} \) can be expressed as \( 2(1-\varepsilon_a/\varepsilon_m)20 \) \( \frac{dn_{y3}}{dE_0} \). The dispersion relation, Eq. (4), by taking differentiation of the equation with respect to $E_0$. Combining the two, the effective index change in the slit region can be expressed as

\[
\frac{dn_{y3}}{dE_0} \Delta n_{y3} = \frac{1}{n_{y3}} \left[ \frac{1}{2} k_0 \sqrt{\varepsilon_m w} - \left( n_{y3}^2 - \varepsilon_m \right)^{1/2} \right] \times \left( 1 - \frac{\varepsilon_a}{\varepsilon_m} \right) \frac{2d}{w}.
\]

(5)

Given these expressions for the effective index changes and the dispersion effects, we can calculate the wavelength shift from the different regions. Calculation shows that the dispersion effect on the top surface of metal is negligible, i.e., \( L_1(n_{y1}/d\lambda) \ll 1 \), in the first term of the denominator of Eq. (2). Substituting \( (dn_{y1}/dE_0)\Delta n_{y1} \) in Eq. (2) with the expression in Eq. (3), and \( (dn_{y3}/d\lambda) \) in Eq. (2) with the one derived from Eq. (4), we can calculate the wavelength shift of the transmission peak caused by analyte adsorption on the top surface of the metal. Similarly, we can calculate the wavelength shift caused by adsorption in the slit region. This process involves the effective index in the slit region, $n_{y3}$, and we obtain its value referring to Fig. 3(a), which shows $n_{y3}$ values calculated for a broad range of slit width. For the given structure and materials system characterized in this work, we assume $L_1=300$ nm, $L_3=150$ nm, $w=40$ nm, $\lambda=680$ nm, $d=1.5$ nm, $\varepsilon_m=2.1$, $\varepsilon_a=1.0$, $\varepsilon_m=-19.1+11.2$, and $dn_{el}/d\lambda=-0.068$. Calculation shows that the slit region contributes 13 nm to the wavelength shift of the transmission peak while the top surface contributes 0.3 nm to the shift. The total shift of 13.3 nm calculated from this formula is in reasonable agreement with the measurement (11 nm) shown in Fig. 1. The analysis clearly reveals that the slit region provides efficient transduction of ambient index change into a spectral shift of optical transmission, while the planar top surface of metal makes a very minor contribution. Sensitivity of this nanoslit-based SPR sensing can be further enhanced by reducing the slit width [Eq. (5)] and/or by increasing the slit depth [Eq. (2)]. Figure 4 shows the sensitivity calculated at 680 nm wavelength for different slit width of a Ag nanoslit array (with grating period of 360 nm and slit depth of 190 nm).

In summary, chemical modification of nanostructured metal surfaces that allow nanoscale confinement of plasmonic fields is a promising approach to developing a new class of SPR sensors that will enable high sensitivity sensing and extremely small miniaturization of SPR devices.

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2. In other versions of surface plasmon sensing based on the Kretschmann configuration, the intensities of scattered and transmitted fields are used to determine the thickness and dielectric constant of an unknown coating. See, e.g., T. A. Leskova, A. A. Maradudin, and W. Zierau, Opt. Commun. 249, 23 (2005), and references therein.
16. $\Delta n_{el}$ is determined from a formula that equates the total amount of polarization charge change induced by analyte adsorption to that with a uniform increment of ambient dielectric constant: $\int_{0}^{\infty} \rho_{el} (\tilde{E}-\bar{E}) d\bar{E}=\int_{0}^{\infty} \rho_{el} \tilde{E} d\bar{E}$. $\varepsilon_0$ is the free-space permittivity. $E$ and $\tilde{E}$ are the electric fields (the normal component to the metal surface) in the dielectric region before and after analyte adsorption, respectively. The electric field in the analytic layer is $\rho_{el} \tilde{E}$ times the electric field in the ambient dielectric and assumed to be constant across the analytic layer thickness, $d$. Assuming negligible perturbation of the fields outside the analytic layer, $\Delta n_{el}$ is calculated as $\frac{1}{2} (1-\varepsilon_a/\varepsilon_m) \frac{d\lambda}{\lambda}$. $\gamma_d$ is the decay constant in the ambient dielectric and is expressed as $\frac{k_{el} \varepsilon_m}{\varepsilon_a} \gamma_d = \frac{1}{2} \varepsilon_a^{1/2} \varepsilon_m^{1/2}$.
19. $\Delta n_{el}$ is determined by equating the total amount of polarization charge change induced by analyte adsorption to that with a uniform increment of ambient dielectric constant in the gap region: $\int_{0}^{\infty} \rho_{el} (\tilde{E}-\bar{E}) d\bar{E}=\int_{0}^{\infty} \rho_{el} \tilde{E} d\bar{E}$. The electric field $E$ is assumed to be constant in the gap region.