High sensitivity sensors made of perforated waveguides

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Abstract: Sensors based on surface plasmons or waveguide modes are at the focus of interest for applications in biological or environmental chemistry. Waveguide-mode spectra of 1 μm-thick pure and perforated silica films comprising isolated nanometric holes with great aspect ratio were measured before and after adhesion of streptavidin at concentrations of 500 nM. The shift of the angular position for guided modes was nine times higher in perforated films than in bulk films. Capturing of streptavidin in the nanoholes is at the origin of that largely enhanced shift in the angular position as the amplitude of the guided mode in the waveguide perfectly overlaps with the perturbation caused by the molecules. Hence, the device allows for strongly confined modes and their strong perturbation to enable ultra-sensitive sensor applications.

OCIS codes: (160.6030) Silica; (240.6680) Surface plasmons; (240.6690) Surface waves; (260.3910) Metals, optics of; (310.2790) Guided waves.

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1. Introduction

Surface plasmon resonances (SPR) is a powerful phenomena for real time detection of bio-molecules in a label-free environment. For the excitation of SPRs, the Kretschmann (Fig. 1)

#77200 - $15.00 USD Received 17 November 2006; revised 12 January 2007; accepted 21 January 2007

configuration is often employed [1]. Briefly, a TM-polarized beam is directed onto the base of a glass prism at an angle necessary for total internal reflection. On the base a suitable metallic thin film is deposited. The electric field couples with the charge density oscillation of the free electrons in the metal and excites a surface plasmon. The surface plasmon causes an evanescent field outside the film whose amplitude decays exponentially away from the metal surface. If an additional dielectric layer is incorporated onto the metal film, the incident light excites likewise weakly guided modes in this waveguiding structure. Both waveguide modes and SPR are simultaneously observed as a sudden drop of reflectivity, as shown in Fig. 2(a). Comparable to the experimental constraints, the structure here consists of a glass prism n_{Prism} = 1.846 on which a gold film (h_{Au} = 50 nm, n_{Au} = 0.166+3.15 i) and a dielectric layer (h_{SiO2} = 500 nm , n_{SiO2} = 1.479) were deposited, where h and n were film thickness and refractive index, respectively. Medium on the transmission side is water (n = 1.333) and the used wavelength was λ = 633nm. Both TE and TM polarization exhibit waveguide modes up to the first or zero order, respectively. A plasmon is observed for TM polarization only. Modes are excited, if the tangential wave vector component matches to the wave number of a guided mode. As guiding losses for waveguides modes are significantly smaller, their line width is superior as compared to the SPR. Perturbing the dielectric environment changes the dispersion of the modes and causes a shift in the angle necessary for their excitation. Very high sensitivity can be expected if the overlap of the modal distribution with external stimuli is maximized. This is not easily achieved for the waveguide modes, as their field amplitudes are concentrated in the volume [Fig. 2(b)]. Nevertheless, their use for sensors is appealing as shifts could be easily detected due to their narrow line width. Full widths at half maximum of TE0, TE1 and TM0 modes are 0.04˚, 0.12˚ and 0.33˚, respectively. Thus, we chose a TE0 mode in the present work.

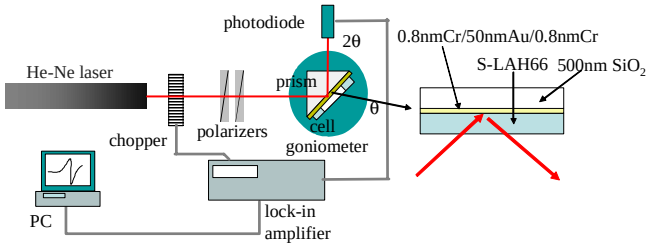

Fig. 1. Experimental arrangement for the measurement in Kretschmann geometry.

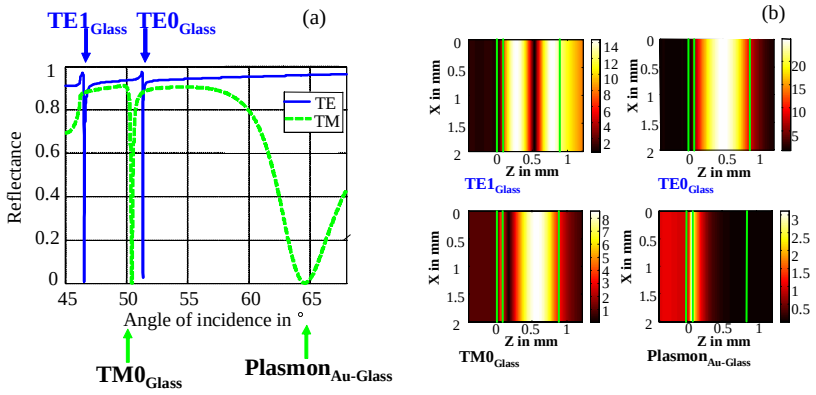

Fig. 2. (a). Calculated reflectivity as a function of the angle of incidence and the polarization for a typical sample as employed in the present investigations. Dips in the reflectivity are associated to be guided modes in the waveguide or to surface plasmon. (b). Amplitudes of excited guided modes. Glass prism, gold film, silica glass and water are lined from left to right. Each boundary is presented by a green line. Scale bars of the field strengths were shown on each right hand side.

#77200 - $15.00 USD Received 17 November 2006; revised 12 January 2007; accepted 21 January 2007

A higher sensitivity of such sensors is already achieved, by increasing the surface of the detector. Porous anodic alumina films are commonly employed to enlarge the surface because of their well-ordered nanostructure self-organizes when aluminum films are anodized in an acid electrolyte causing pores at sufficient diameters. These pores run straight through the film parallel to each other. The pore sizes are dictated by a combination of the applied voltage used for the anodization and the solutions employed. For example, self-ordering takes place at 25 V in sulfuric acid solution, at 40 V in oxalic acid solution, and at 195 V in phosphoric acid solution, leading to pore sizes of 65 nm, 100 nm, and 500 nm, respectively [2]. Disadvantage of such an approach is the impossibility to obtain pores with arbitrary diameters. It has been reported that porous aluminum films may be employed simultaneously as deposition templates and as highly sensitive detectors of processes within the pores [3, 4]. Also porous silicon has been used as a bio-sensing material [5].

We will report here on a strategy to perforate dielectric waveguides to enhance significantly the sensitivity of the sensor as firstly, the perturbation of the modes by adsorbed molecules is enlarged and secondly, their adhesion surface is increased. Silica coat is mechanically and environmentally stable. The holes in the insulator are created in the following way: the passage of an atomic particle through an insulator results in the creation of a cylindrical, latent nuclear track that extends along a straight line corresponding to the path of the atomic particle [6]. The presence of tracks is revealed after etching in a suitable solution. However, the shape of the etched hole is often not cylindrical, but conical, with the largest diameter being near the surface. This is a consequence of the etching rate in the latent track being comparable to the general etching rate in the unirradiated region. Musket *et al.* have used vapor etching of ion tracks to create high aspect ratio, isolated cylindrical holes through ~600 nm-thick films of thermally grown silica on silicon [7]. In the present study, we have adopted the vapor etching technique to create cylindrical holes through silica waveguides. Excitation of the surface plasmon and waveguide modes are experimentally observed as very sharp dips in reflectivity when measured as a function of the incident angle. Au must be needed, otherwise we cannot observe waveguide mode. The adhesion of streptavidin molecules onto the surface and into the holes inside the waveguide causes a strong shift in the measured angular position of the modes. We found a nine times increase of the shift for the perforated waveguides as compared to bulk waveguides at the expense of only slightly larger line widths. The line width of those modes is only negligible larger due to enhanced scattering at the surface of the holes increasing the guiding losses. As the diameter of the holes was in the order of a few tens of nanometers only, the modes experience effective material parameters for the waveguide material and will not interact sensitive on the fine details of the holes. Incorporation of streptavidin causes a significant change in the optical properties of the waveguide material.

2. Experimental

As glass substrate and prism, we used S-LAH66 glass (Ohara Co., Ltd.) with a high refractive index of 1.769 [8]. To ensure adhesion of a 50 nm Au layer on the substrate, first a ~0.8 nm Cr layer was deposited on the surface. On top of the gold film again a ~0.8 nm Cr layer was deposited by thermal evaporation (R-DEC Co., Ltd., Japan). Finally, a 500nm thick-waveguide layer of a-SiO_x film was deposited on the Cr/Au/Cr films. To improve the optical performance of the film, the structure was tempered at 600 ˚C for 24 h. Rutherford backscattering measurement revealed the x in a-SiO_x to be in the vicinity of 2. Thus, hereinafter we call the film silica.

Ion bombardment to perforate the waveguide was performed at room temperature at a residual pressure below 1×10^{-4} Pa. The 12 UD Pelletron tandem accelerator at the University of Tsukuba was employed with 150 MeV Au^{14+} ions. To avoid overlap of the individual cylindrical holes, very low ion fluency was required. This was achieved by diffusing the ion beam through an aluminum foil in forward scattering geometry. 150 MeV Au^{14+} was reduced to 137 MeV Au^{30+} by passage through the Al foil. We performed vapor etching experiments with 20% hydrofluoric acid (HF). Influence of various liquid T_L and sample T_S temperatures

#77200 - $15.00 USD Received 17 November 2006; revised 12 January 2007; accepted 21 January 2007

was examined and T_L = 19 ˚C and T_S = 30 ˚C were obtained as a best condition. Changing the temperature allowed for control over the hole sizes.

The substrate glass was mounted on a prism to form an optically contiguous medium. A He-Ne laser operating at 632.8 nm was used in subsequent measurements and a polarizer selected for either TE- or TM-polarization. We also clamped a Teflon flow cell onto the exposed film to permit injection and extraction of the desired dielectric medium/reagents. To observe the optical waveguide modes, reflectivity was measured at a constant temperature of 20.8˚C against incident angle.

Figure 3 illustrates the chemical surface modification procedure to ensure adhesion of molecules. At first, the surface of silica was modified by silanol groups. It has been reported that the number of surface silanol groups is increased in an alkali solution [9]. Thus, 3-aminopropyltriethoxysilane (3APT) was bound with a silanol groups by immersing the silica waveguide substrates in 0.5 vol% 3APT ethanol solution for 3 h. The 3APT-modified substrate was rinsed with ethanol and dried in a stream of nitrogen gas and then immersed in 0.5 mM 5-[5-(N-succinimidyloxycarbonyl)pentylamido]hexyl D-biotinamide (biotin-$(AC_5)_2$-OSu) solution in 1/15 M PBS buffer (pH 7.4) for amide-coupling with the 3APT layer. Biotin-$(AC_5)_2$-OSu) was used for streptavidin capture in the presence of phosphate buffer solution (PBS) [10].

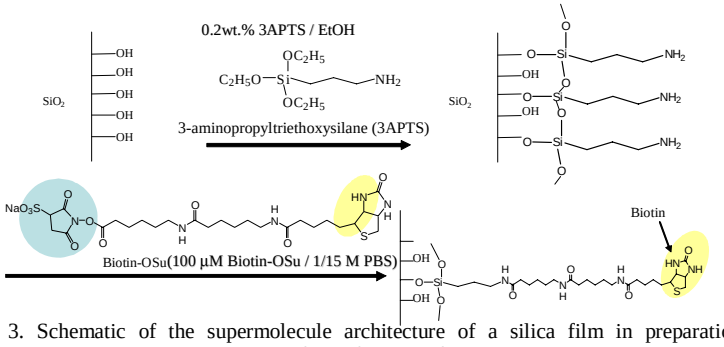

Fig. 3. Schematic of the supermolecule architecture of a silica film in preparation for streptavidin capture. A hydrophilic surface of a silica film was obtained in alkali solution. 3-aminoprophyltriethoxysilane (3APT) was used as the silane coupling agent. The 3APT-modified substrate was immersed in 0.5 mM 5-[5-(N-succinimidyloxycarbonyl) pentylamido]hexyl D-biotinamide (biotin-$(AC_5)_2$-OSu) solution in 1/5 M PBS buffer for amide coupling with the 3APT layer.

3. Results and discussion

SEM images of the fabricated samples provided sufficient evidence that cylindrical holes were etched into the 500nm-thick silica films (Fig. 4.) These holes with a diameter of ~ 50 nm resulted from vapor etching followed by rinsing in distilled water and drying. The hole density was estimated to be 5.0 (± 0.8) $\times 10^8$ cm^{-2} as deduced from SEM images, which is consistent with the experimentally counted fluence of 5.0 (± 0.2) $\times 10^8$ cm^{-2} using a Faraday cup.

Waveguide modes can be excited in the silica waveguide. The waveguide mode spectrum shifts when the silica waveguide film is exposed to a solution containing biotin of 500 μM. Figure 5(a) shows reflectivity against incident angle in the vicinity of the TE0 mode obtained on the as-prepared silica film before (black circles) and after (red circles) immersion in biotin solution. The central line shift in the as-prepared sample case was less than 0.01˚ and merely noticeable. The angular resolution in this experiment was 0.01˚. Figure 5(b) shows the reflectivity vs. angle around the same mode obtained on porous silica film with a number of 1 x 10^{10} cm^{-2} holes, 500nm deep and 50 nm in diameter. The black and red circles indicate the spectra before and after immersion in biotin solution. The central line shift was dramatically increased up to 0.14˚. It was found that the remaining dip intensity was increased by the creation of holes and the line width was likewise increased slightly. Both observations are easily attributed to an increase of the guiding losses of the modes due to additional light

#77200 - $15.00 USD Received 17 November 2006; revised 12 January 2007; accepted 21 January 2007

scattering at the etched holes and also due to the chrome on the metal film and the APT modification of silica. Reduction of refractive index with increase of holes in waveguide introduced wider dips and much smaller contrast of in off- and on-resonance reflectance. Better spectrum can be obtained with controlling thickness of waveguide and metals.

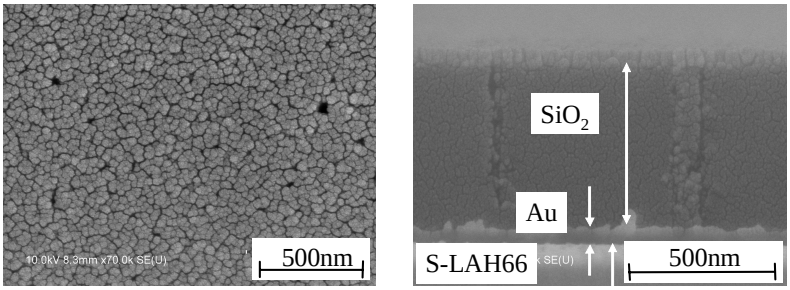

Fig. 4. Top (left) and cross-sectional (right) view of a particular silica films. Here 137 MeV Au^{30+} ion bombardment was performed at a fluence of 5×10^{8} cm^{-2} followed by vapor etching.

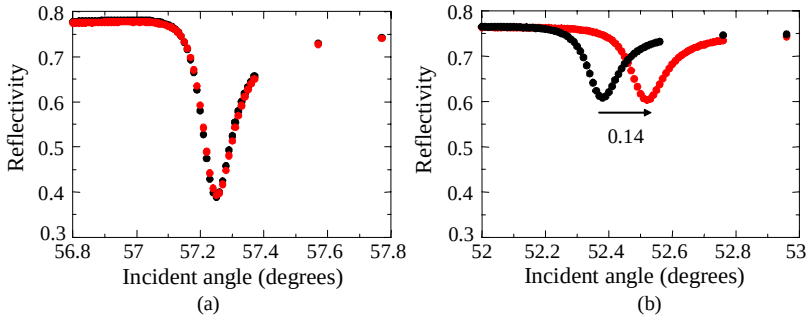

Fig. 5. (a). TE0 mode of the waveguide before (black) and after (red) modification with 500-μM biotin. Shift of the dip position was less than 0.01˚. (b). TE0 mode of the silica waveguide substrate with a density of $1x10^{10}$ cm^{-2} holes before and after modification with 500-μM biotin.

Figure 6 shows angular dependent reflectivity for a TE0 mode before and after capturing streptavidin of 500 nM. For the silica waveguide before creation of pores, dip shift was estimated to be 0.06 ˚. The sample having 1×10^{10} holes/cm² was fragile and it was not successful to measure the spectrum after biotin-streptavidin bindings. When a number of 7 x 10^{9} cm^{-2} holes were created in the silica waveguide, central position of the dip shifted dramatically by 0.53 ˚. Materials may not reach the bottom of the hole but the vicinity of the maximum of field distributions of the guided modes that are concentrated inside the waveguide. Additional waveguides with increased hole densities were fabricated and the TE0 spectra were measured. The relationship between dip shift due to capturing of streptavidin and hole density was examined. Change in reflectivity at a constant angle ($\Delta R/R$) could be estimated from the TE0 spectra. For example, reflectivity at 53.56˚ was estimated from Fig. 6(b) to be 0.51 before and 0.78 after capturing of streptavidin. Based on those values, we evaluated the relative change in reflectivity ($\Delta R/R$) with respect to the unexposed sample. $\Delta R/R$ values are plotted against hole-density in Fig. 7. It was found that the dip shift increases with number of holes. The $\Delta R/R$ value reached a maximum above 3 x 10^{9} cm^{-2}. Saturation is observed, as the line width of the unexposed compared to the exposed spectra are no more overlapping. Such a shift is hardly to achieve with conventional plasmon based sensors.

Shift of SPR peak position due to biotin-streptavidin bindings was reported as 360ng/cm^2 per 0.01° [11]. When surface was filled with streptavidin molecules of 5nmϕ, mass of streptavidin can be estimated as 400ng/cm^2, which is close to the value reported in [11]. It is

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impossible to compare the displacement of the angle per biotin-streptavidin bindings between SPR and TE0 mode because SPR cannot be excited in the silica waveguide. Moreover, surface area of porous silica in the laser beam spot is 7.88cm^2 which is much larger than 0.03cm^2 of non-porous silica. The relative change in reflectivity ($\Delta R/R$) of SPR and TE0 mode were calculated at 0.2% and 2% per 0.01° shift, respectively. From the calculation, it was firmed up that approach of the present work was better than SPR. We expect the sensor chips to be able to detect impurities of ppb order.

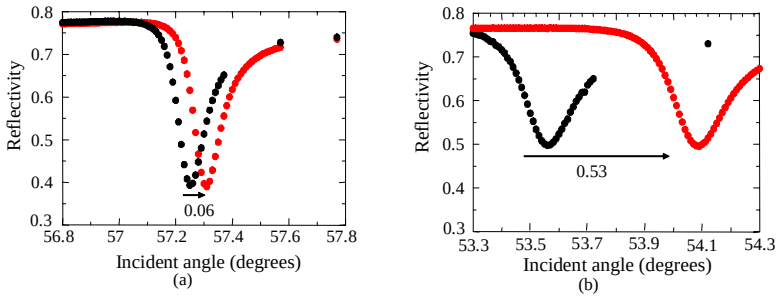

Fig. 6. TE0 modes of the waveguide modified with biotin. Black and red circles denote reflectivity before and after capture of 500 nM streptavidin. (a). No holes. (b). 7×10^9 holes cm^{-2}.

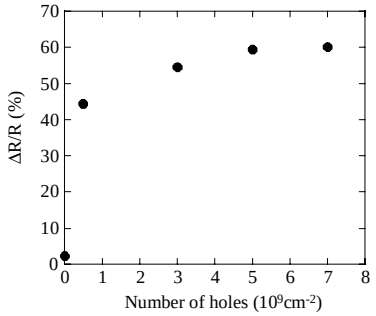

Fig. 7. Relative change in reflectivity ($\Delta R/R$) of TE0 against hole density in the waveguide.

4. Summary

In the present experiment, a genuine configuration for the detection of low levels of biomolecules was explored that employs guided modes in perforated dielectric waveguides. It was found that a concentration of 500 μM of biotin, which cannot be detected employing the bulk silica waveguide, could be detected with the perforated silica waveguide. Also by capturing streptavidin of 500nM, the angular position of the waveguide modes for the TE0 was shifted up to 0.53. The shifts exceed significantly the line width of the resonance itself, hence allowing for unprecedented change in the reflectivity for such low concentration of molecules to be detected. The high sensitivity of the present sensor derives from a maximization of the overlap of modal volume and the molecules to be detected via the nanometer sized holes that were created in the waveguides. The present approach will contribute significantly towards the development of ultra-high sensitive sensors in various fields.

Acknowledgments

C. Rockstuhl, would like to thank the Canon-Foundation Europe for financial support.

#77200 - $15.00 USD Received 17 November 2006; revised 12 January 2007; accepted 21 January 2007