

Experimental study of sensitivity enhancement in surface plasmon resonance biosensors by use of periodic metallic nanowires

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We have experimentally confirmed sensitivity enhancement of a nanowire-based surface plasmon resonance (SPR) sensor structure. Gold nanowires with periods of 200 and 500 nm were fabricated, respectively, by electron-beam and interference lithography on a gold/SF10 substrate. Sensitivity enhancement was measured to be 44% compared with a conventional thin-film-based SPR structure for nanowires of 200 nm period and 31% for 500 nm when evaluated using ethanol at a varied concentration. This result is consistent with numerical data. Surface roughness is responsible for sensitivity reduction by more than 10%. More significant sensitivity improvement can be achieved by inducing strong localized plasmon coupling with finer nanowires. © 2007 Optical Society of America

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Various optical properties have been reported of metallic nanostructures both theoretically and experimentally. One of the most interesting phenomena is the excitation of localized surface plasmons (LSPs), which depends on size, shape, and environment of the nanostructures and leads to enhancement of local electromagnetic fields [1–3]. In contrast with a conventional surface plasmon resonance (SPR) biosensor on a thin film, localized and highly enhanced plasmons can interact with biochemical binding events close to a noble metal nanostructure and subsequently cause a larger shift of resonant LSP modes [4,5]. The field enhancement has been investigated as a way to enhance the sensitivity limit that has long plagued SPR biosensors. While most of the earlier studies used nanoparticles for convenience of synthesis, we have considered nanowires as an alternative structure to excite LSPs for improved reproducibility. In our previous studies, metallic nanowire-mediated SPR biosensors were shown numerically to enhance the sensitivity by more than an order [6,7]. The sensitivity enhancement was associated with a surface-limited increase of reaction area and structural perturbation of periodic nanowires on a thin gold film. The perturbation prompts propagating surface plasmons to interfere with excited localized plasmons, which achieves local field enhancement by resonantly exciting LSP modes and coupling effects between the LSP modes.

In this Letter, we experimentally support theoretically studied sensitivity characteristics of a nanowire-mediated SPR biosensor. Initially, periodic gold nanowires with a 500 nm period were patterned on a 40 nm thick gold film by interference lithography. This technique can fabricate periodic structures over a large area at a grating period (Λ) that is as small as half the wavelength (λ) of light source, i.e., $\Lambda = \lambda/2 \sin(\theta/2)$ with θ as an interference angle. In Fig. 1(a), a thin gold film was sputtered on a SF10

glass substrate after a chromium layer was applied to increase the adhesion of the gold film to the substrate. Ar gas (40 sccm) was used under a 4 mTorr chamber pressure at 250 W RF power for gold and at 300 W DC power for chromium. Azobenzene copolymer (57042-7, Sigma Aldrich, St. Louis, MO) was used as a photoresponsive polymer. It was dissolved in tetrahydrofuran at a concentration of 3%. The

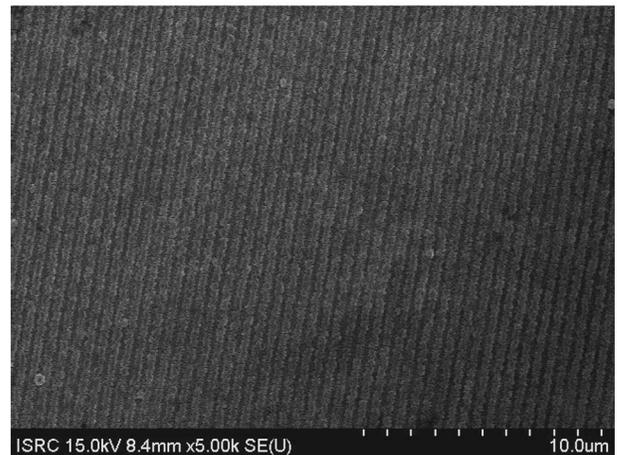
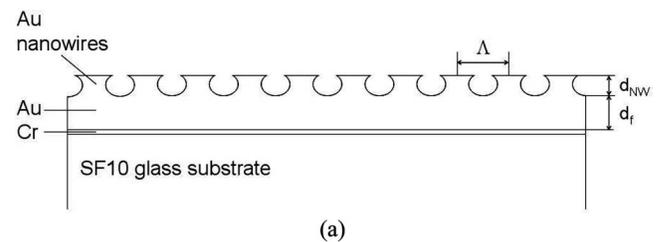


Fig. 1. (a) Schematic profile of a nanowire-based SPR chip and (b) scanning electron image of the sample with $\Lambda = 500$ nm.

polymer film, coated on a gold layer by spin coating, was dried for 6 h at 70°C and irradiated by two coherent beams of a 488 nm sapphire laser (100 mW) at $\theta=60^\circ$. Patterns on the copolymer were transferred as gold nanowires after uniform dry etching of the copolymer followed by gold sputtering for planarization and dry-etching processes, and finally removing the entire copolymer. The etch rate of gold using Cl_2 (56 sccm), CF_4 (30 sccm), and O_2 (10 sccm) gases was 400 Å/min for a 0.1 Torr pressure at 200 W.

For effective sensitivity performance, gold nanowires have been intended to take roughly an inverse trapezoidal profile with $\Lambda=500$ nm, 250 nm width (i.e., fill factor $f=50\%$), and $d_{\text{NW}}=60$ nm [6]. The total effective area where nanowires were formed was approximately 5 mm \times 5 mm. Despite good uniformity over a large area as shown in Fig. 1(b), however, severe dry-etching processes caused substantial roughness on the surface. The effect of roughness on the sensitivity has been reported as degrading [8], which is to be discussed in more detail subsequently.

For sensitivity characteristics at a smaller period, nanowire samples with $\Lambda=200$ nm were fabricated on a thin gold film by electron-beam lithography. The substrates were spin coated by a 100 nm thick photoresist (SAL601) film. The regions exposed to an electron beam were chemically dissolved, and the resulting photoresist layer was used as a mask for dry etching of a gold film. Following uniform dry etching, an isotropic etching process using 30% aqua regia ($\text{HCl}:\text{HNO}_3=3:1$) was applied to induce an inverse trapezoidal nanowire cross section. Finally, a residual photoresist layer was removed by means of a plasma asher. After these processes, we produced one-dimensional gold nanowires arranged on 40 nm thick gold/SF10 glass substrates. The nanowire width was 45 nm ($f=22.5\%$), and $d_{\text{NW}}=15$ nm. The sample area was 1.5 mm \times 1.5 mm.

A conventional thin-film-based SPR structure was also evaluated for a comparison study. For the conventional structure, a 40 nm thick gold film and a 2 nm thick layer of chromium were deposited on a SF10 glass substrate.

The characterization of the nanowire-mediated SPR biosensor structure was performed with an in-house optical setup using an intensity-based angular interrogation scheme. Note that the sensitivity performance of an intensity-based scheme was reported as comparable with or superior to that of a phase-sensitive SPR biosensor [9]. Our setup employs a polarized 10 mW He–Ne laser ($\lambda=0.6328$ μm) and dual rotation stages (URS75PP, Newport, Irvine, CA), pre-aligned for the sensor chip and a calibrated photodiode (818-UV, Newport, Irvine, CA), with a nominal resolution of 0.002°. In terms of minimum measurable refractive index difference, this corresponds to the sensitivity of an optical setup estimated to be in the range of $\Delta n \sim 1 \times 10^{-6}$ for a conventional SPR structure with a gold thin film. The sensitivity limit of the setup can be easily improved by employing a rotation stage with enhanced angular resolution or using a more powerful laser with a sensitive detector.

Although measured SPR characteristics for a conventional and a nanowire-based SPR chip are not presented here, the experimental results are well matched with simulations based on rigorous coupled-wave analysis [10]. The incidence angles at resonance (θ_{SPR}) for a medium of pure water were 54.32°, 58.28°, and 65.59° for a conventional and a nanowire-based SPR chip with $\Lambda=200$ nm and $\Lambda=500$ nm, respectively.

The sensitivity of the nanowire-based SPR structure has been evaluated by measuring the dependence of θ_{SPR} on ethanol concentration. Ethanol concentration was measured by an Abbe refractometer (Leica Mark II, Reichert Analytical Instruments, Depew, NY). The measured refractive index change was $\Delta n=0.0017$ with an increase of the concentration of ethanol mixture from 0% for pure water ($n=1.33382$). Figure 2(a) shows that the resonance angle shift ($\Delta\theta_{\text{SPR}}$) for a conventional SPR scheme is 0.132°, and for a nanowire-mediated SPR structure of $\Lambda=500$ nm, it is $\Delta\theta_{\text{SPR}}$ is 0.173°. An error bar is larger for the sample of periodic nanowires, since the nanowire pattern is not perfectly uniform in the sample area shown in Fig. 1(b). However, linear regression analyses show that the resonance shift is fairly linear both with and without nanowires. The sensitivity enhancement factor (SEF), defined as the

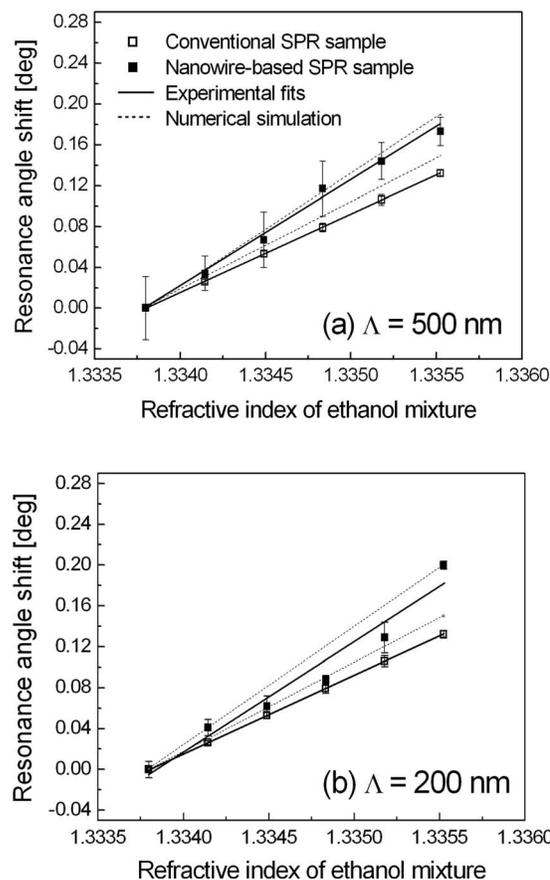


Fig. 2. $\Delta\theta_{\text{SPR}}$ of a nanowire-based SPR chip at (a) $\Lambda=500$ nm and (b) $\Lambda=200$ nm, in comparison with a conventional one without nanowires. The solid and dotted lines represent linear fits of experimental and numerical results, respectively.

ratio $\Delta\theta_{\text{SPR}}$ (with nanowires)/ $\Delta\theta_{\text{SPR}}$ (without nanowires), was measured to be 1.31, indicating a 31% increase in sensitivity. The measurement is in good agreement with numerical data calculated by rigorous coupled-wave analysis for an identical configuration. For the nanowire-based SPR sample, discrepancies in the linear fits of the SEF between the experimental and simulation data are attributed mainly to the surface roughness of the gold film and nanowires. The numerical data suggest that the surface roughness reduced the sensitivity at least by 10%. The roughness is also responsible for spatial variances in the sensitivity results.

The measured sensitivity enhancement of the nanowire-based SPR chip with a 200 nm period is presented in Fig. 2(b). When the concentration of ethanol varies, $\Delta\theta_{\text{SPR}}=0.20^\circ$, and the SEF value was determined from linear regression analysis to be 1.44, i.e., 44% sensitivity improvement. Relatively simple fabrication processes induce smaller error deviation and less sensitivity degradation than with the SPR sample of $\Lambda=500$ nm. Also, the broadening that often accompanies LSP-based SPR characteristics was not observed for the sample with a 200 nm period. SEF = 1.44 is not a disruptive performance *per se*. However, considering that the nanowire periods used in this study were 500 and 200 nm, the results promise the possibility of significant sensitivity improvement through simple reduction of the period. Earlier studies indicated that optimized performance in terms of sensitivity (SEF close to 30) and SPR characteristics can be obtained with nanowires of $\Lambda=50$ nm [7]. On the other hand, it is quite interesting to see that sensitivity is enhanced even at $\Lambda=500$ nm and $\Lambda=200$ nm by forming extremely narrow nanogrooves, although in this case amplification of fields is mostly localized near nanogrooves where relatively few tar-

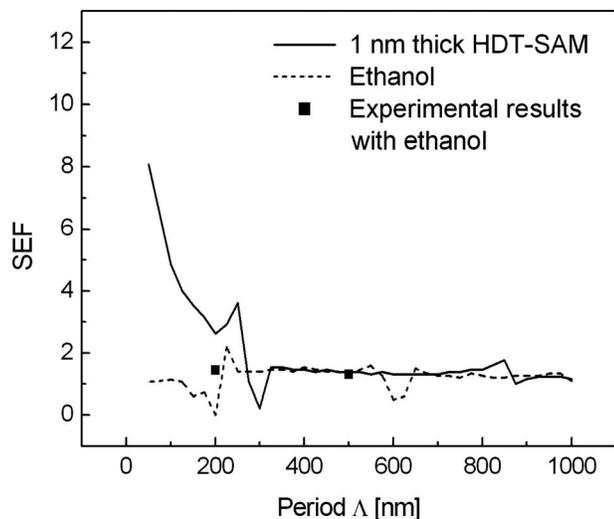


Fig. 3. Calculated SEF as a function of nanowire periods, assuming a rectangular profile with $f=50\%$. The squares represent measured data.

get molecules can be diffused. It should also be noted that SEF is a function of target analytes. For example, Fig. 3 presents the SEF calculated for a 1 nm thick 1,6-hexanedithiol self-assembled monolayer (SAM), $n_{\text{SAM}}=1.52643$, in air environment, compared with the SEF of ethanol mixture at various periods of nanowires. Although the calculation assumed a rectangular profile with $f=50\%$, the results are consistent with experimental data. The sensitivity of ethanol tends to underperform that of using SAMs with a large refractive index difference, despite relatively thin film thickness. Thus, we believe that the data presented in this study are close to the worst-case results and that the sensitivity can be improved significantly using finer nanowires for specific analytes involving biological SAMs. Note that the dips in Fig. 3 are associated with phase retardation caused by the presence of analytes [7].

In summary, we have fabricated an SPR structure and nanowires of $\Lambda=500$ nm based on interference lithography and $\Lambda=200$ nm by use of electron-beam lithography. By using varied ethanol concentration, SEFs of 1.31 and 1.44 were measured over a thin-film-based conventional structure. The results are consistent with theoretical data. It is expected that use of finer nanowires can further enhance the sensitivity.

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