

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/7760130>

Surface Plasmon Sensor Based on the Enhanced Light Transmission through Arrays of Nanoholes in Gold Films

ARTICLE *in* LANGMUIR · JULY 2004

Impact Factor: 4.46 · DOI: 10.1021/la0493621 · Source: PubMed

CITATIONS

454

READS

71

4 AUTHORS, INCLUDING:



Alexandre G. Brolo

University of Victoria

155 PUBLICATIONS 4,885 CITATIONS

SEE PROFILE



Reuven Gordon

University of Victoria

204 PUBLICATIONS 4,497 CITATIONS

SEE PROFILE



K.L. Kavanagh

Simon Fraser University

217 PUBLICATIONS 5,088 CITATIONS

SEE PROFILE

Surface Plasmon Sensor Based on the Enhanced Light Transmission through Arrays of Nanoholes in Gold Films

Alexandre G. Brolo,^{*,†} Reuven Gordon,[‡] Brian Leathem,[§] and Karen L. Kavanagh[§]

Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, British Columbia, Canada V8W 3V6, Department of Electrical and Computer Engineering, University of Victoria, P.O. Box 3055, Victoria, British Columbia, Canada V8W 3P6, and Department of Physics, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia, Canada V5A 1S6

Received March 11, 2004. In Final Form: April 17, 2004

Arrays of nanoholes in a gold film were used to monitor the binding of organic and biological molecules to the metallic surface. This technique is particularly sensitive to surface binding events because it is based upon the resonant surface plasmon enhanced transmission through the array of nanoholes. The sensitivity was found to be 400 nm per refractive index unit, which is comparable to other grating-based surface plasmon resonance (SPR) devices. The array of nanoholes is well suited for dense integration in a sensor chip. Furthermore, the optical geometry is collinear, which simplifies the alignment with respect to the traditional Kretschmann (reflection) arrangement for SPR sensing.

Surface plasmon resonance (SPR) sensors are widely used in biomedical and biochemical research for the characterization and quantification of binding events.^{1,2} Commercial SPR devices generally operate in total internal reflection mode using the Kretschmann configuration.¹ SPR-based sensors that operate in transmission geometry have been established for ultrathin gold island films³ and nanoparticles immobilized on glass.⁴ In this work, we will demonstrate that a periodic square array of sub-wavelength holes on gold films can be utilized as a SPR sensor. This new sensor also operates in transmission mode, allowing for a simpler collinear optical arrangement and providing a smaller probing area than the typical Kretschmann configuration.

The transmission of normally incident light through arrays of sub-wavelength holes is enhanced at the wavelengths that satisfy the SPR conditions given by^{5,6}

$$\lambda^{\text{SP}}(i, j) = p(i^2 + j^2)^{-1/2} \left(\frac{\epsilon_{\text{eff}} \epsilon_m}{\epsilon_{\text{eff}} + \epsilon_m} \right)^{1/2} \quad (1)$$

where p is the periodicity of the array, i and j are integers, ϵ_{eff} is the effective dielectric constant at the metal–dielectric interface, and ϵ_m is the dielectric constant of the metal. The surface plasmon (SP)-mediated transmission is several orders of magnitude higher than expected from Bethe's law for the transmission of light through sub-wavelength apertures.⁷ The enhanced transmission is

accompanied by strong field localization and has potential for applications in several fields, such as quantum information processing,⁸ microscopic optical components,⁹ wavelength conversion,¹⁰ and nanolithography.¹¹ The role of the SP in this interesting phenomenon has been confirmed by a series of experimental^{12,13} and theoretical^{14,15} works. The dependence of the SPR on the dielectric constant of the adjacent medium has been explored by changing the nature of the liquid in contact to the array of sub-wavelength holes.¹⁶ The refractive index at the metal interface was also modulated by applying an alternating voltage to a liquid crystal in contact to the surface, leading to a selective control of the wavelength of the transmitted light through the manipulation of the optical properties of the adsorbate.¹⁷ Arrays of sub-wavelength holes in Ni have also been used to promote enhanced transmission in the mid-IR range.¹⁸ The path length for light absorption is significantly increased, as demonstrated by the 100-fold enhancement in the IR spectrum for 1-dodecanethiolate adsorbed at these arrays of nanoholes in Ni.¹⁸ Although these results^{16–18} strongly suggest that these devices can be used as chemical sensors, there is no report in the literature so far on the utilization

* Corresponding author: e-mail address, agbrolo@uvic.ca; telephone, (250) 721-7167; fax, (250) 721-7147.

[†] Department of Chemistry, University of Victoria.

[‡] Department of Electrical and Computer Engineering, University of Victoria.

[§] Simon Fraser University.

(1) Nice, E. C.; Catimel, B. *BioEssays* **1999**, *21*, 339–352.

(2) Vo-Dinh, T.; Cullum, B. *Fresenius' J. Anal. Chem.* **2000**, *366*, 540–551.

(3) Kalyuzhny, G.; Vaskevich, A.; Schneeweiss, A.; Rubinstein, I. *Chem. Eur. J.* **2002**, *8*, 3849–3857.

(4) Malinsky, M. D.; Kelly, K. L.; Schatz, G. C.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2001**, *123*, 1471–1482.

(5) Ebbesen, T. W.; Lezec, H. J.; Ghaemi, H. F.; Thio, T.; Wolff, P. A. *Nature* **1998**, *391*, 667–669.

(6) Thio, T.; Ghaemi, H. F.; Lezec, H. J.; Wolff, P. A.; Ebbesen, T. W. *J. Opt. Soc. Am. B* **1999**, *16*, 1743–1748.

(7) Bethe, H. A. *Phys. Rev.* **1944**, *66*, 163–182.

(8) Altwischer, E.; van Exter, M. P.; Woerdman, J. P. *Nature* **2002**, *418*, 304–306.

(9) Vallius, T.; Jefimovs, K.; Turunen, J.; Vahimaa, P.; Svirko, Y. *Appl. Phys. Lett.* **2003**, *83*, 234–236.

(10) Nahata, A.; Linke, R. A.; Ishi, T.; Ohashi, K. *Opt. Lett.* **2003**, *28*, 423–425.

(11) Shinada, S.; Hashizume, J.; Koyama, F. *Appl. Phys. Lett.* **2003**, *83*, 836–838.

(12) Lezec, H. J.; Degiron, A.; Devaux, E.; Linke, R. A.; Martin-Moreno, L.; Garcia-Vidal, F. J.; Ebbesen, T. W. *Science* **2002**, *297*, 820–822.

(13) Degiron, A.; Lezec, H. J.; Barnes, L.; Ebbesen, T. W. *Appl. Phys. Lett.* **2002**, *23*, 4327–4329.

(14) Martin-Moreno, L.; Garcia-Vidal, F. J.; Lezec, H. J.; Pellerin, K. M.; Thio, T.; Pendry, J. B.; Ebbesen, T. W. *Phys. Rev. Lett.* **2001**, *86*, 1114–1117.

(15) Martin-Moreno, L.; Garcia-Vidal, F. J.; Lezec, H. J.; Degiron, A.; Ebbesen, T. W. *Phys. Rev. Lett.* **2003**, *90*, 167401.

(16) Krishnan, A.; Thio, T.; Kim, T. J.; Lezec, H. J.; Ebbesen, T. W.; Wolff, P. A.; Pendry, J.; Martin-Moreno, L.; Garcia-Vidal, F. J. *Opt. Commun.* **2001**, *201*, 1–7.

(17) Kim, T. J.; Thio, T.; Ebbesen, T. W.; Grupp, D. E.; Lezec, H. J. *Opt. Lett.* **1999**, *24*, 256–258.

(18) Willians, S. M.; Stafford, A. D.; Rodriguez, K. R.; Rogers, T. M.; Coe, J. V. *J. Phys. Chem. B* **2003**, *107*, 11871–11879.

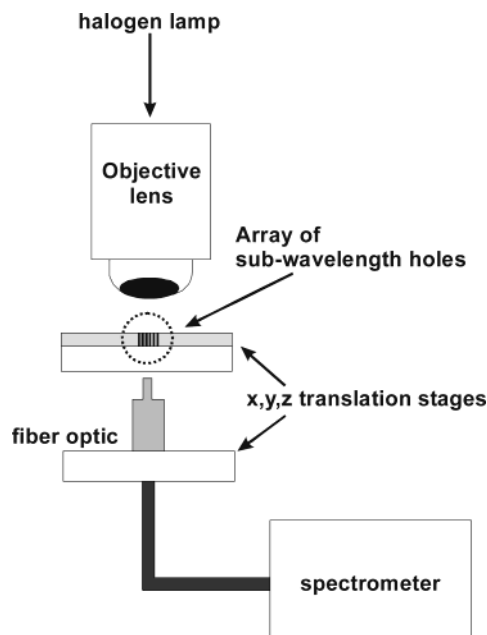


Figure 1. Experimental setup for light transmission measurements through the arrays of sub-wavelength holes.

of the enhanced transmission as an analytical probe to monitor surface binding events at the molecular level. Here, we quantify the sensitivity of the nanohole SPR configuration to detect surface binding of organic and biological molecules.

The arrays of sub-wavelength holes were fabricated and imaged using a FEI 235 dualbeam focused ion beam and field emission scanning electron microscope. The gallium ion beam was set to 30 keV for milling with a milling rate of $1.6 \text{ nm } \mu\text{s}^{-1}$ for gold and a beam current of 300 nA. The diameters of the sub-wavelength holes were 200 nm, and the gold films were 100-nm thick. Six square arrays with sub-wavelength holes of different periodicities p (distance between the holes) equal to 510, 545, 590 (3 arrays), and 618 nm were produced. White light transmission through the arrays was measured using an Olympus BHS-M metallurgical microscope coupled to an Ocean Optics USB-2000 miniature fiber optic spectrometer. A schematic of the apparatus is shown in Figure 1. The halogen lamp from the microscope was the near-IR source, and a $100\times$ objective lens was used. All spectra were obtained using normal incident and unpolarized light. The acquisition time was 200 ms, and 20 accumulations were recorded. The slides (containing the array of sub-wavelength holes) were cleaned prior to each experiment by using an oxygen plasma cleaner and an ultrasound bath. The procedure involved etching the gold surface in the plasma oven for 20 min followed by sonication in ultrapure water (Barnstead Nanopure Diamond water purification system).

A scanning electron microscope image of a typical array used in this work is shown in Figure 2A. Figure 2B is an expanded view of the full $16 \mu\text{m} \times 16 \mu\text{m}$ array presented in Figure 2A. Figure 2C shows the transmission spectra of white light through three arrays of sub-wavelength holes with different periodicities cleaned using the procedure just described. The peak at 580 nm in curve a of Figure 2C is related to the (2,0) Au-glass resonance, and the peaks at 657, 597, and 652 nm in curves a–c are due to the (1,0) mode at the Au-air interface. The minima that appear in all spectra just before the resonances are attributed to Wood's anomaly, which occurs when the diffracted light emerges parallel to the metal surface.⁶

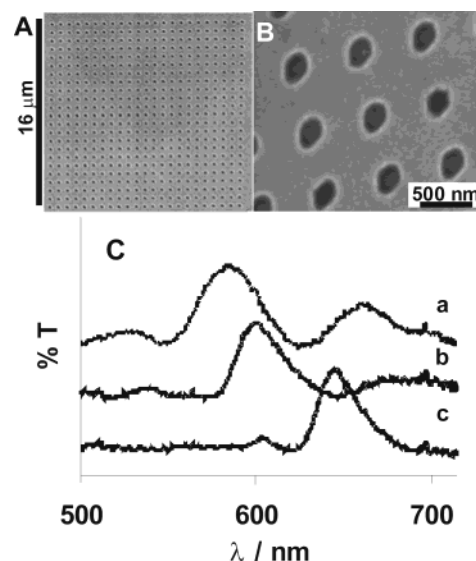


Figure 2. (A and B) Scanning electron microscopy images of a typical array of sub-wavelength holes. The image in part B is an enlargement of the array presented in part A. (C) Normalized transmission spectra of white light through three arrays of sub-wavelength holes. All arrays were patterned in a 100-nm-thick gold film deposited on the glass slide, and the diameters of the holes were about 200 nm. The lattice parameters (periodicities) of arrays a–c were 618, 545, and 590 nm, respectively.

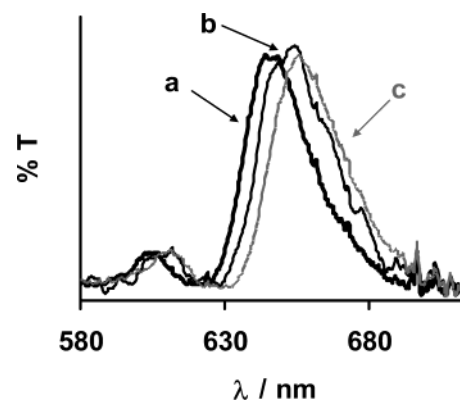


Figure 3. Normalized transmission spectra of normally incident white light through an array of sub-wavelength (200-nm diameter) holes on a 100-nm-thick gold substrate deposited on a glass slide. (a) Bare (clean) Au surface; (b) Au modified with a monolayer of MUA; (c) Au-MUA modified with BSA.

The shape (aspect ratios) of the nanoholes was also varied on different templates to explore the influence of this fabrication parameter on the optical properties of the transmitted light, and these results are presented elsewhere.¹⁹

After being characterized, the slides were immersed in a 1 mM ethanoic solution of 11-mercaptoundecanoic acid (MUA) for 24 h. They were then dried using a pure nitrogen stream, and the normal transmission spectra were measured. The Au surfaces modified with MUA were further immersed in 100 μM aqueous solution of either bovine serum albumin (BSA) or cytochrome c (cyt c) for 6 h and dried, and the transmission spectra were measured.

Figure 3 shows the transmission spectrum of normally incident white light through one of the arrays after

(19) Gordon, R.; Brolo, A. G.; McKinnon, A.; Rajora, A.; Leathem, B.; Kavanagh, K. L. *Phys. Rev. Lett.* **2004**, *92*, 037401.

successive surface modifications. The spectrum shown in Figure 3a presents a sharp resonance from the (1,0) mode of the air–bare metal interface at 645 nm. The spectrum in Figure 3b, obtained after the metallic surface was modified with a monolayer of MUA, shows that the maximum in the transmission shifted to 650 nm. An additional shift in the SPR to 654 nm, as shown in Figure 3c, was observed after the protein adsorption to the MUA layer. Similar shifts in the wavelength of the maximum transmission were also obtained using cyt c. After the protein modification, the gold slide was removed and cleaned in a plasma oven for 20 min. After that, it was immersed in pure water and placed in an ultrasound bath for another 20 min, removed, and dried. The transmission spectrum obtained from the clean surface coincided with the one observed in Figure 3a. The average shifts from the clean surface considering all six slides were 4 ± 1 nm after modification with MUA, 9 ± 1 nm after modification with BSA, and 8 ± 1 nm after modification with cyt c.

The shifts in the SPRs, as shown in Figure 3, are related to changes in the effective dielectric constant at the metallic interface due to molecular adsorption. The effective dielectric constant at the modified interface can be estimated by performing a weighted average within the extension l_d of the evanescent SP mode into the dielectric (z direction), according to²⁰

$$\epsilon_{\text{eff}} = \frac{2}{l_d} \int_0^\infty \epsilon(z) \exp\left(-\frac{2z}{l_d}\right) dz \quad (2)$$

The expected shift in the SPR from the bare gold due to the formation of a monolayer of MUA calculated from eqs 1 and 2 (using 1.7 nm as the thickness of the MUA layer, 1.45 as the refractive index,²¹ and 200 nm as a constant decay length l_d of the SP mode into the dielectric)²² was about 4 nm, which is in very good agreement with the observed shift from Figure 3. The experimental shift in the wavelength observed after the protein adsorption was always smaller than estimated using ϵ_{eff} for a multilayer structure (using the parameters and procedure described in ref 20). The reason for this effect is yet unknown, but a similar discrepancy between the observed and calculated shifts in SPR resonances was observed for polypeptide adsorption onto gold islands immobilized in glass.⁴

It is clear from Figure 3 that the arrays of sub-wavelength holes on gold act as a highly sensitive sensor to the detection of molecular adsorption at both monolayer and multilayer levels. Similarly to other SPR configurations, the good sensitivity to surface binding is the result of the tightly confined SP mode.²² It is precisely this SP mode that allows for the enhanced transmission resonance in the arrays of nanoholes.⁵ The measured sensitivity of these arrays to refractive index variation was 400 nm RIU⁻¹ (RIU = refractive index unit). This value is comparable to those calculated for a grating-based SPR (300–630 nm RIU⁻¹),²³ for gold colloids (66.5 nm RIU⁻¹) and gold nanoshells (328.5 nm RIU⁻¹) in aqueous solution,²⁴ and for substrates prepared by nano-sphere lithography (ca 150 nm RIU⁻¹).⁴ The absolute sensitivity is, however, smaller than that obtained by fixed-angle SPR using the Kretschmann configuration (between 3100 and 8000 nm RIU⁻¹).²⁰ The advantage of using the nanohole array is that it provides a smaller sensing probe (given by the surface area of the array); consequently, the analytical response is generated by a smaller absolute number of molecules and leads to better spatial resolution than typical SPR devices. The transmission geometry is also advantageous for device implementation because it allows for easy optical alignment. Another unique feature of the substrates presented here is the presence of the Wood's anomaly, which induces an asymmetry in the transmitted resonance (the rise of the peak edge is steeper in the lower wavelength range). The Wood's anomaly also depends on the dielectric constant of the interface⁶ and shifts under molecular adsorption. Thus, a shift in the peak edge can also be used to monitor binding events.

In summary, we have demonstrated the application of arrays of nanoholes in gold films as SP-based sensors for the adsorption of biomolecules. The monolayer sensitivity of this substrate is comparable to other grating-based SP systems. The array of sub-wavelength holes investigated here are only a few micrometers in length, and the detection was made in transmission mode. These features render this substrate ideal for miniaturization and integration as detection systems in microfluidics architectures and lab-on-chip devices.

Acknowledgment. This work was supported by NSERC Discovery and equipment grants from CFI and BCKDF. This collaboration has been facilitated by the CAMTEC and PCAMM research centers.

LA0493621

(20) Jung, L. S.; Campbell, C. T.; Chinowsky, T. M.; Mar, M. N.; Yee, S. S. *Langmuir* **1998**, *14*, 5636–5648.

(21) Hanken, D. G.; Jordan, C. E.; Frey, B. L.; Corn, R. M. *Electroanal. Chem.* **1998**, *20*, 141–225.

(22) Homola, J.; Yee, S. S.; Gauglitz, G. *Sens. Actuators, B* **1999**, *54*, 3–15.

(23) Moharam, M. G.; Gaylord, T. K. *J. Opt. Soc. Am. A* **1986**, *3*, 1780–1787.

(24) Sun, Y.; Xia, Y. *Analyst* **2003**, *128*, 686–691.