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研究課題名(和文) ナノキャビティの表面プラズモン閉じ込め効果を用いた疾病センサーの開発

研究課題名(英文) light confinement in plasmonic nanocavities for use as biosensor

## 研究代表者

J・J Delaunay (Delaunay, Jean-Jacques)

東京大学・工学(系)研究科(研究院)・准教授

研究者番号：80376516

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研究成果の概要(和文)：本研究の目的は、癌や心疾患などの疾病の早期診断を可能にする、小型かつ安価なセンサーを実現することである。ナノキャビティ(ナノスケールの厚みを有する金属側壁からなる溝)内に表面プラズモンを閉じ込めることで、微量の検体から、疾病バイオマーカーを高感度に検出する。ナノキャビティ内に光を閉じ込め、ナノキャビティの底面と側面に生じる表面プラズモンを結合させることで、共鳴に必要な構造を簡略化、センサーの小型化を実現する。

研究成果の概要(英文)：The purpose of the research project is to demonstrate a small-size and low-cost sensor for the early diagnosis of diseases. A very sensitive detection technique of biomarkers is being developed using confined surface plasmons in nano-cavities operating on small sample volumes. Perfect light confinement in nano-cavities is possible when high-aspect-ratio U-shaped cavities are used to couple the cavity ridge hot spots with the scalable U-cavity resonances. Under the condition of coupled resonance, light is fully trapped in intense optical vortices and confined on the extended U-shaped cavity surfaces. This strong resonance generates sensitive reflectance dips. The light confinement in the nano-cavity is realized for a finite number of adjacent nano-cavities, so small sample volumes can be used. The reported perfect light confinement in the nano-cavities observed as a strong and sharp resonance is used in biochemical marker detection in a protein-ligand scheme.

研究分野：ナノマイクロ加工

キーワード：メタマテリアル・表面プラズモン

### 1 . 研究開始当初の背景

Containing costs of the health care system is a major issue of today's society. One of the most promising strategies is to develop early diagnosis of diseases. For this purpose, the development of a fast, sensitive and cheap detection technique of disease biomarkers is required. Measuring the optical response of a device based on surface plasmons provides a fast and sensitive means to detect biomarkers in the form of a wavelength shift of the surface plasmons resonance dip. Investigations into the potential of the surface plasmons generated by periodic subwavelength hole arrays in the detection of disease biomarkers in breath have been conducted. Unfortunately, the hole arrays generate surface plasmons propagating in the plane of the hole arrays over long distances, so that large sensor areas are required. Furthermore, hole arrays do not produce sharp resonance dips required for a high sensitivity. Thus the hole arrays requires large amounts of sample (blood, breath) and lack sensitivity. In this research proposal, nano-cavities (high-aspect-ratio sidewalls with nano-size width) are used to trap light and form surface plasmons on the cavity wall surfaces. Thus, the surface plasmons are no more allowed to propagate, but are confined in the nano-cavities. An ultra-small detection area with a minute amount of sample is used for sensing and a high sensitivity is achieved thanks to the sharp resonance dip provided by the nano-cavities.

### 2 . 研究の目的

The purpose of the research project is to demonstrate a small-size and low-cost sensor for the early diagnosis of diseases. A very sensitive detection technique of biomarkers should be developed using confined surface plasmons in nano-cavities operating on small sample volumes. The objectives of this research proposal are:

- Understand the physics of the coupling of surface plasmons in a nano-cavity.
- Quantify the theoretical sensitivity of the nano-cavity optical response to biomarkers.
- Verify experimentally the potential of nano-cavity in the detection of biomarkers.

### 3 . 研究の方法

The design of the cavity was performed using the following optical simulation tools. The finite-difference time-domain (FDTD) technique was used to understand the light energy flux in the cavity and the rigorous coupled-wave (RCWA) analysis to calculate the reflectance spectra from which the sensitivity to deposited biomaterials was

computed. Light energy flux in a nano-cavity was found to exhibit a vortex pattern, evidence for the light being trapped in the cavity. The surface plasmons (SP) are confined (i.e. non-propagating) in the cavity on the sidewalls and at the bottom. The cavity reflectance spectrum calculated by RCWA showed a sharp dip, corresponding to the cavity resonance at which light is trapped. The dip shift upon deposition of biomarkers on the cavity walls was simulated by adding a thin layer of biomaterials on the cavity walls. The effect of the number of cavities on the sensitivity of the dip shift was also reported.

The fabrication sequence of the high-aspect-ratio cavities was as follows. A Si substrate was first cleaned by an O<sub>2</sub> plasma treatment following a hydrophilic process. A photoresist is spin coated on the Si substrate. A lithography process is performed with a mask aligner. After a development process, gold is conformally sputtered on the developed resist pattern. Sputtered gold film on the top of the developed resist and gold film on the top of substrate is removed by reactive ion etching with a gas mixture of Ar and CF<sub>4</sub>. Finally, the remaining resist between the gold sidewalls is removed by O<sub>2</sub> plasma treatment.

The fabricated cavity sensors were characterized by near-infrared spectrometry. The zero-order reflectance spectra was recorded as a function of the light incidence angle. The surrounding environment of the cavities was controlled: both dry air and liquid environments were tested. For the liquid environment, a transparent cell containing the cavity sensor in a solution was used in combination with standard solvents such as water, ethanol, and alkanes.

The effect of biomaterial coating on the cavity walls was evaluated by measuring the reflectance spectrum before and after the attachment of biomolecules (first antibody coating, then antigen binding). For this purpose, the wavelength of the resonance dip was estimated from the reflectance spectrum and the dip shift upon binding of biomolecules was determined. It should be noted that due to the high modulation in reflectance provided by the nano-cavities, a high signal-to-noise ratio was achieved and no special procedure was needed to filter the measured spectra (e.g., Savitzky-Golay filter).

### 4 . 研究成果

We clarified the mechanism of light confinement in the proposed nano-cavities and applied this knowledge to the design of the nano-cavities for biomaterial sensing. The mechanism of light trapping in the

nano-cavities was described in our recent publication *Advanced Optical Materials*, 2, 522-528, 2014). We show that light is confined in the nano-cavities by coupling plasmonic modes to scalable cavity modes and, therefore, the resonance of the nano-cavities can be controlled by varying the geometrical parameters of the cavities. This property enables tuning of the nano-cavity resonance wavelength in the near infrared region in which detection of biomaterials is most efficient. We fabricated the designed nanocavities and obtained a good agreement between the simulated properties of the designed nano-cavities and the fabricated nano-cavities.

The sensitivity of the proposed U-shaped nano-cavities was quantified in terms of the shift in the resonance wavelength. The change in the wavelength of the resonance reflectance dip of the nano-cavities was first investigated by varying the refractive index of the surrounding of the nano-cavities. Moreover, the ability of the nano-cavities to detect biomarkers was tested using a protein ligand scheme by observing the change in the resonance wavelength upon the selective attachment of proteins on the nano-cavity surfaces.

Finally a design enabling low-cost fabrication of the sensitive cavity structure was proposed, tested and published (*Applied Physics Letters*, 105, 061112, 2014).

#### 5. 主な発表論文等

(研究代表者、研究分担者及び連携研究者には下線)

〔雑誌論文〕(計 6 件)

(1) Ya-Lun Ho, Alejandro Portela, Yaerim Lee, Etsuo Maeda, Hitoshi Tabata, Jean-Jacques Delaunay, “Hollow Plasmonic U-Cavities with High-Aspect-Ratio Nanofins Sustaining Strong Optical Vortices for Light Trapping and Sensing,” *Advanced Optical Materials*, Vol. 2, 6, 522-528, 2014 (back cover and selected as best of *Advanced Optical Materials* 2014 by the Editor).

(2) Pascal Delange, Ya-Lun Ho, Jean-Jacques Delaunay, “Plasmon focusing in short gold sphere nanochains for surface enhanced Raman scattering,” *Applied Optics*, 52, 8809-8816, 2013. (selected by the Editors, Andrew Dunn and Anthony Durkin, for publication in the *Virtual Journal for Biomedical Optics*)

(3) Ya-Lun Ho, Jean-Jacques Delaunay, “Light Trapping in Finite Arrays of Metallic U-shaped Cavities for Sensing with High Figure of Merits,” *Photonics Technology Letters*, vol. 26,

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〔学会発表〕(計 3 件)

(1) J.-J. Delaunay, Y.-L. Ho, Y. Lee, E. Maeda, “Localized surface plasmons coupled to U-shaped cavity for high sensitivity bio-sensing applications,” 15th International Symposium on Olfaction and Electronic Nose, EXCO Daegu, Korea, July 2-5, 2013 (oral).

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(3) Y.-L. Ho, Y. Lee, E. Maeda, and J.-J. Delaunay, “High-aspect-ratio plasmonic U-shaped nano-cavity with high sensitivity and figure of merit,” IEEE International Conference on Nano/Micro Engineered and Molecular Systems (IEEE-NEMS) (Hawaii, USA), T2G, April, 2014 (Oral).

〔図書〕(計 0 件)

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〔その他〕  
ホームページ等  
<http://scale.t.u-tokyo.ac.jp/research/index.html>

## 6. 研究組織

### (1) 研究代表者

J-J Delaunay (ジェイ ジェイ ドロネー)  
東京大学・大学院工学系研究科・准教授  
研究者番号：80376516

### (2) 研究分担者

田畑 仁 (タバタ ヒトシ)  
東京大学・大学院工学系研究科・准教授  
研究者番号：00263319

藤川 茂紀 (フジカワ シゲノリ)  
九州大学・カーボンニュートラル・エネルギー国際研究所 准教授  
研究者番号：60333332

前田 悦男 (マエダ エツオ)  
東京大学・大学院工学系研究科・助教  
研究者番号：60644599

### (3) 連携研究者

岡本 美孝 (オカモト ヨシタカ)  
千葉大学・医学研究科・教授  
研究者番号：40169157