



Original research article

SPPs characteristics of Ag/SiO₂ sinusoidal nano-grating in SERS application

Cheng Xiao*, Zhibin Chen, Mengze Qin, Dongxiao Zhang, Lei Fan

Department of Electronic and Optical Engineering, Shijiazhuang Campus of Army Engineering University, Shijiazhuang, Hebei 050003, China

ARTICLE INFO

Article history:

Received 5 January 2018

Received in revised form 19 April 2018

Accepted 19 April 2018

Keywords:

Surface enhanced Raman spectroscopy

Surface plasmon polaritons

Sinusoidal grating

Absorbance

ABSTRACT

Surface enhanced Raman spectroscopy (SERS) substrate aimed at providing robust and reproducible enhancements is discussed. The periodic sinusoidal SiO₂ grating followed by silver evaporation is proposed for the creation of reproducible and effective SERS substrate based on surface plasmon polaritons (SPPs). Detailed optical properties theoretical and simulation studies with finite difference time domain (FDTD) are performed to achieve intense excitation SPPs. Substrate parameters such as period, amplitude of sinusoidal grating and thickness of silver layer, detailed excitation light parameters such as wavelength, polarization state and polarization angle are explored. It's found that the enhancement factor (EF) of SERS is proportional to the efficiency of excitation SPPs. Optimal SERS response can be realized by assembling the substrate and excitation light parameters appropriately. The substrates are fabricated and an extra SERS effect of the optimal Ag/SiO₂ sinusoidal nanograting is demonstrated by the experiments.

© 2018 Elsevier GmbH. All rights reserved.

1. Introduction

Surface enhanced Raman spectroscopy (SERS) is a powerful analytical technique, enabling identify molecules with their vibrational spectra at extreme low concentration [1]. It owns the potential applicability in numerous practical fields, such as biological sensing [2], trace analysis [3] as well as cancer diagnosis and detection of pesticides, explosives and drugs [4]. High enhancement of the near field intensity is the key factor for ultrasensitive SERS realization [5].

Surface plasmons can be excited as surface waves that are bound to, and propagate along the interface between metal and dielectric half spaces. They are frequently referred to as “surface plasmon polaritons” (SPPs). The second type of surface plasmons are those excited in metal nanoparticles. These are termed “localized surface plasmons” (LSPs), as the fields are enhanced in sub-wavelength regions around the particles [6]. Noble metallic nanoparticles are high effective SERS substrates, due to the giant enhancement of the local electromagnetic field generated by LSPs [7,8]. However, uncontrolled nanoparticles aggregation leads to poor reproducibility of SERS signal and seriously limits its wide application. One way is to process substrates with hot spots distribution in order [9]. This can be achieved by ordered arrangement of nanoparticles in different structures [10] or by deposition of thin metal layer onto previously patterned template [11,12]. Through the precise tailoring of template, plasmon modes can be guided and optimal SERS excitation wavelength can be tuned [13,14]. In order to improve the LSPs effect, nanoparticles coated with MoS₂ sub-micrometer sphere-ZnO nanorod hybrid photocatalysts

* Corresponding author.

E-mail address: xc_nanking@163.com (C. Xiao).

was synthesized [15]. Besides, ultrathin monolayer graphene was adopted as well-defined subnanospacer between noble metallic nanoparticles and metal film [16], such as an all-copper sandwich system with depositing Cu nanoparticles onto a graphene sheet [17], hybrid nanostructures composed of graphene or other two-dimensional nanomaterials and plasmonic metal components [18].

As a rule, better periodicity of the prime template results in a higher SERS signal intensity and more appropriate signal uniformity [19]. Highly ordered 2D gold or silver arrays with subwavelength dimension [20], which enable one to excite Bloch wave SPPs. In this case, because of surface polariton excitation and propagation, electric field enhancement occurs not only at the local places, but also spreads over the surface with a spatially modulated intensity [21]. Therefore, large area electromagnetic enhancement occurs on the surface, which strongly contrasts with the traditional hot spots [22]. With this method, the poor reproducibility of SERS substrate can be eliminated. In addition, coupling effect exists in LSPs and SPPs, a double-resonance SERS system was prepared by assembling gold nanoparticles separated by a MoO_3 nanospacer from an silver grating film [23].

But in fabrication process of the previous ordered SPPs and LSPs SERS substrates, ordered arrangement of nanoparticles or prefabricate templates are time-consuming and costly. Besides, the large area ordered SERS substrates fabrication is also a difficulty with the traditional method. However, the sinusoidal silver grating in this work could be fabricated by the process of two beam laser interference of photoresist. This method has no need of prefabricate templates and the larger area ordered SERS substrates can be fabricated through large area exposure. In this work, a potentially reliable SERS substrate based on periodic sinusoidal SiO_2 grating followed by silver evaporation is offered. From theoretical and simulation points of view, the excitation SPPs performance of this substrate is researched. Substrate parameters and excitation light parameters are studied detailedly, such as period amplitude of sinusoidal grating, thickness of silver layer, wavelength, polarization state and polarization angle.

2. Model preparation and FDTD numerical simulation

Based on the dielectric functions of noble metals [24], we investigate why propagating SPPs can exist at dielectric-metal interfaces. The grating is a mean to couple to SPPs. In order to excite SPPs, one must overcome the momentum mismatch between excitation light propagating within a dielectric medium and SPPs propagating at the interface of a metal and dielectric [25]. Diffraction gratings with periodicity P can provide wavevector components in the plane of the surface with magnitude $K = 2\pi n/P$, n is a integer [25,26]. For a fixed P , a properly chosen excitation light wavelength λ_0 [27]:

$$\lambda_0 \approx \frac{P}{n} \sqrt{\frac{\varepsilon_{\text{metal}}(\lambda_0)\varepsilon_{\text{dielectric}}}{\varepsilon_{\text{metal}}(\lambda_0) + \varepsilon_{\text{dielectric}}}} \quad (1)$$

where $\varepsilon_{\text{metal}}$ and $\varepsilon_{\text{dielectric}}$ are the dielectric constant of metal layer and above dielectric, respectively. λ_0 can excite SPPs with k_{spp} [26,28]:

$$k_{\text{spp}} = \left| k_0 \sin \theta \pm n \frac{2\pi}{P} \right| \quad (2)$$

where θ is the incident angle of excitation light. We establish the original model of sinusoidal Ag/ SiO_2 nano-grating with excitation light 785 nm. This wavelength is extensively adopted in SERS detection. In order to choose the appropriate grating period, we carry out calculations treating the metal as silver with a Drude plus two-pole Lorentzian form for its dielectric constant [29],

$$\varepsilon_{\text{metal}}(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} - \sum_{m=1}^2 \frac{g_m \omega_m^2 \Delta\varepsilon}{\omega^2 - \omega_m^2 + i2\gamma_m\omega} \quad (3)$$

where for silver, $\varepsilon_{\infty} = 2.3646$, $\omega_p = 8.7377$ eV, $\gamma = 0.07489$ eV, $\Delta\varepsilon = 1.1831$, $g_1 = 0.2663$, $\omega_1 = 4.3802$ eV, $\gamma_1 = 0.28$ eV, $g_2 = 0.7337$, $\omega_2 = 5.183$ eV, $\gamma_2 = 0.5482$ eV. The insertion of Eq. (3) into Eq. (1), when $n = 1$, we can obtain the grating period is 770 nm, as shown in Fig. 1. It's obviously that grating period is proportional to wavelength of excitation light in SPPs condition.

For further study SERS characteristic of sinusoidal Ag/ SiO_2 nano-grating, the FDTD Solutions is used to simulate the consequent SPPs phenomenon generated with plane wave excitation. We model the electromagnetic response of the structures as shown in Fig. 2(a). The electric $\mathbf{E}(x,y,z,t)$ and magnetic $\mathbf{H}(x,y,z,t)$ fields are represented on discrete, staggered grids and propagated in time using a leap-frog algorithm [30].

Referring to the coordinate systems in Fig. 2(a), structure model consists of two layers (silver and SiO_2), with period P , thickness d of silver layer, amplitude A of sinusoidal grating. The medium above the silver layer is air. Periodic boundary conditions in x and y are imposed on unit cells consistent with each structure to simulate the gratings. Perfectly matched layers (PMLs) are used to absorb field components at the grid edges in the $\pm z$ -directions [30]. The excitation light is a x -linearly polarized plane wave normal to the silver layer surface injected using plane wave approach. A frequency-domain field and power monitor is placed at the cross profile of the structure to record the near field intensity. In order to calculate the transmittance and reflectance of sinusoidal silver layer, further two frequency-domain field and power monitors are placed above silver layer and in SiO_2 layer, respectively. Relatively fine grid spacings set with 5 nm, and simulation time with 1000 fs is applied for well converged results.

Download English Version:

<https://daneshyari.com/en/article/7223534>

Download Persian Version:

<https://daneshyari.com/article/7223534>

[Daneshyari.com](https://daneshyari.com)