Slow plasmon-polaritons in a bilayer metallic structure revealed by the lower-energy resonances of surface-enhanced Raman scattering

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Abstract: Apart from the main plasmon-polariton resonance of the surface-enhanced Raman scattering (SERS) occurring at 480 - 530 nm, an additional resonance was observed for substrates with two silver layers separated by a dielectric layer which support extra plasmon modes with decreased group velocities. The novel SERS resonance is shifted towards lower energies and has comparable amplitude, its exact energy position being determined by the thickness of the dielectric interlayer. The experimental findings provide a ground for the engineering of SERS-substrates with the spectral position of the additional resonance matched with the photon energy of the pump laser over a fairly wide range of laser wavelengths.

1. Introduction

The phenomenon of the surface-enhanced Raman scattering (SERS) enables a very prominent application in the field of plasmonics at optical frequencies occurring thanks to the existence of surface plasmon-polariton excitations in thin metallic films [1–5]. A strong localization of the electromagnetic field near a film surface and a corresponding huge local field enhancement ensures a dramatic increase in the photon scattering response of e.g. organic molecules on the film surface [6–11]. The process of transformation of the transverse electromagnetic radiation (typically, laser emission) into the surface plasma waves requires the transfer of additional momentum \( k \), which can be supplied by the surface in case it is composed of metallic granules that are smaller than the photon wavelength. For very thin silver films that are frequently used in SERS-sensing, this requirement is usually fulfilled since for thicknesses less than 5-7 nm the silver film consists of separate granules with a characteristic planar size of 20-30 nm [12,13]. The resonant plasma frequency of such silver islands corresponds to the light wavelengths about 450-550 nm, and this fact is responsible for the enhancement maximum of the optical response from the silver-based SERS substrates taking place for the laser wavelength close to 500 nm. At the same time, apart from the enhanced Raman signal occurring in the mentioned spectral range, photoexcitation of organic molecules at these laser energies frequently brings about a very prominent luminescence signal preventing fast and reliable detection of the Raman scattered signal. The most obvious method of suppression this parasitic luminescence consists in reducing the pump photon energy below the characteristic optical transition energies in the molecule. However the fixed frequency of a dimensional plasmon resonance in silver granules does not permit any significant shifting the pumping laser frequency to the red or infrared wavelengths range. Therefore, there exists a great demand in engineering the SERS-structures that would realize an extra plasmon mode with resonance frequencies shifted appreciably to lower energies. The physical concept that proves to be very useful in achieving the aforementioned goal relies on...
the emergence of additional plasmon-polariton modes in a metal-dielectric structure with two and more metallic layers [14–16], in contrast to the case of a single metallic film surrounded by a dielectric medium that supports less plasmon-polariton modes. A very important prerequisite is the dependence of the dispersion (and velocity) of the additional plasmonic waves on the number of metallic layers as well as thicknesses of dielectric layers separating them [15–17]. Therefore, adding extra layers of thick metal near the main granular silver layer and varying the thickness of the dielectric slab separating the metallic layers should enable the tuning of plasmonic modes and thus achieving SERS-resonances at the desired wavelengths.

Early works [15] proposed that in the case of a single metallic layer with a thickness of $d_m$ surrounded on both sides by a vacuum there exist two surface plasmon-polariton modes. They correspond to the in-phase and anti-phase oscillations of charge densities on opposing metal film surfaces, and for the small wave-vectors the group-velocities of both modes approach the speed of light $c$. The situation is substantially different for a metal-insulator-metal (MIM) structure with two metallic layers of thickness $d_1$ and $d_2$ separated by a dielectric slab of thickness $d_{ins}$, the resulting three-layer structure being again surrounded by a vacuum. In this case, owing the increased number of surfaces, the number of plasmonic modes increases significantly up to five, and, most importantly, apart from the two very similar plasmon-polariton modes, there exists an additional mode with a $k \approx 0$ group-velocity much smaller than $c$ which is finely tunable by changing the geometric parameters of the structure: the thicknesses of the metallic and dielectric layers [15–17]. Since the pioneering work by Economou [15] the MIM structures were extensively studied both theoretically and experimentally [18–20], and are being considered as promising building blocks for the engineering of novel micro-scale lasers [21], photodetectors [22] and broadband absorbers [23].

In this paper, we demonstrate the efficient excitation of the slow plasmon-polaritons at optical frequencies in MIM structures and their application to the field of SERS-based sensing. The SERS-active structures were designed to have a silicon monoxide (SiO) dielectric layer of different thicknesses and an additional thick silver layer that were deposited below a conventional granular silver layer. The study shows that, along with the main plasmon-polariton SERS resonance observed in the 480 - 530 nm wavelength range, the proposed structure supports also an additional SERS resonance that is shifted towards lower energies and has comparable amplitude. It was confirmed that the position of that additional SERS resonance is determined by the thickness of the dielectric interlayer separating the metallic layers, which allows tuning the spectral position of the resonance over a fairly wide range. The realized SERS resonance is thus shown to be related to the complementary slow plasmon-polariton mode.

2. Experimental setup

The experimental structures were fabricated as follows. (a) A reference structure without an additional thick silver layer: a 200 nm thick SiO layer with a 6 nm thin silver SERS-overlayer were resistively evaporated on a polished glass substrate. The resulting surface was composed of silver granules with characteristic planar sizes of 20-30 nm. (b) Structures with an additional thick metallic layer: the reference architecture was complemented by a 50 nm thick silver layer buried into the SiO layer at a depth $d_{ins}$ below the upper SERS-active thin silver layer. Five structures with $d_{ins} = 30$ nm, 50 nm, 75 nm, 100 nm and 150 nm were fabricated and investigated. All the structures were similarly spin-coated with a mono-molecular layer of a specific organic substance and then studied with the aid of a Raman spectrometer directly mounted on an optical microscope. To reduce the influence of the chemical nature of the organic substances and clearly elucidate the fundamental physical effect from the additional thick metallic layers, four different analytes were used as Raman-active organic substances: 3,3’, 5,5’ - tetramethylbenzidine (TMB), 4 -aminobenzentiol (4 - ABT), beta-carotene and citric acid. The experimental setup included lasers that enabled Raman measurements at four excitation wavelengths: 488 nm, 532 nm, 568
3. Results and discussion

Figure 1 shows typical SERS spectra measured on the reference SERS substrate (without an additional thick silver layer) for the two analytes: TMB [Fig. 1(a)] and 4 - ABT [Fig. 1(b)] under a photoexcitation by a 532 nm laser. The scattered signal intensity allowed estimation of the SERS enhancement factor of around $10^6$ for these measurements - the value typically achieved for the substrates and the excitation wavelength used [12,13]. It was determined as the ratio of the selected spectral feature intensities under conditions of the SERS-enhancement and without it. In the latter case the analyte was dispensed on a clean glass slide and had much higher thickness as required for the detection of non-enhanced and therefore very weak Raman signals; naturally it also required much higher signal acquisition times. It’s worth mentioning that the experimentally extracted absolute SERS enhancements have always some uncertainty due to the unknown precise thicknesses of the analyte layers, varying conditions like focusing spot size etc. and thus may vary by a factor up to 10. Therefore, in the following we used the normalized SERS enhancement factor to compare the signal enhancement at different excitation and detection wavelengths.

Being inherently a higher-order Raman process [24], SERS phenomenon is dependent on conditions of both the input and output resonances, in other words on the detunings of the incident photon energy and the scattered photon energy from the plasma resonance. Therefore it is very instructive to introduce the concept of the spectral contour of the SERS enhancement factor describing a dependence of the increase in the surface-induced optical response on both the laser energy and the scattered photon energy. In order to investigate the spectral contour of the
SERS enhancement factor, along with using various excitation wavelengths as input resonances, the following set of Raman lines of the four chosen organic substances were selected as output resonances (the corresponding Raman shifts are indicated in meV units):

<table>
<thead>
<tr>
<th>Substance</th>
<th>39.5</th>
<th>61.1</th>
<th>113.6</th>
<th>145.3</th>
<th>163.5</th>
<th>179.1</th>
<th>196.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMB</td>
<td>47.4</td>
<td>64.9</td>
<td>87.0</td>
<td>111.8</td>
<td>131.1</td>
<td>139.4</td>
<td>170.4</td>
</tr>
<tr>
<td>4-ABT</td>
<td>119.4</td>
<td>138.1</td>
<td>183.7</td>
<td>263.6</td>
<td>282.4</td>
<td>308.4</td>
<td>327.1</td>
</tr>
<tr>
<td>beta-carotene</td>
<td>28.2</td>
<td>113.7</td>
<td>170.3</td>
<td>362.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results of measuring the spectral contour of the SERS enhancement factor proved to be practically independent of the analyte chosen and therefore characterized specifically the physical properties of the SERS structures. Thanks to the fact that the analyzed Raman shift values were generally small compared to the variation in the probe laser energies, the resonance SERS enhancement contour combining both the input and output resonances can be fairly well described by a dependence on the output resonance energy only. In the following we'll discuss this simplified yet a very fruitful approach for a characterization of the SERS enhancement factor.

Figure 2(a) shows SERS spectra measured for a monomolecular analyte layer (4 - ABT) on the surface of a reference SERS substrate. The spectra were measured at four different laser wavelengths, the photoexcitation power density was kept the same. It is clearly seen that a SERS enhancement is observed for wavelengths of 488 nm, 532 nm and 568 nm, however it is practically absent for the 647 nm wavelength. This result is well known for the conventional SERS substrates with a 5-6 nm thick upper silver layer [12,13]. Figure 2(b) shows Raman spectra measured under the same experimental conditions (identical analyte, laser power and wavelengths) but acquired on a modified SERS substrate. The only difference of this SERS substrate from the reference one was an additional thick silver layer buried inside the structure at a depth $d_{ins} = 50$ nm from the top SERS-layer. In can be concluded that the SERS efficiency at laser wavelengths of 488 nm, 532 nm and 568 nm remains practically unchanged for a modified SERS-substrate while at a 647 nm wavelength it increases by several orders of magnitude. This finding demonstrates clearly that an addition of another metallic layer gives rise to a new SERS resonance that has comparable amplitude and is shifted towards the lower energies. From now we'll analyze the dependence of the energy shift of that additional resonance on the distance $d_{ins}$ between the two metallic layers.

Figure 3 illustrates the spectral dependencies of the normalized SERS enhancement factor measured for the reference structure [Fig. 3(a)], as well as for three structures with an additional buried metal layer separated from the upper SERS layer by a distance 30 nm [Fig. 3(b)], 50 nm [Fig. 3(c)] and 100 nm [Fig. 3(d)]. As mentioned above, the dependencies are plotted against the absolute value of the output resonance energy. Despite lower intensities of the spectral lines at $\sim 520$ nm in Fig. 2 compared to the $\sim 560$ nm region, the SERS enhancement turned to be higher for the former one, because the non-enhanced Raman spectra (not shown) at $\sim 520$ nm revealed even weaker spectral features compared to the wavelength region around 560 nm. Furthermore, it is clearly seen that the spectral contour of the SERS enhancement factor from the reference structure contains a single SERS resonance and its maximum corresponds to the energy value of 2390 meV (518 nm wavelength); the characteristic resonance half-width is approximately 90 meV. The presence of an additional thick silver layer at a distance $d_{ins}$ keeps the properties of the main resonance practically unchanged: only a slight energy red-shift, about 60 meV, of the resonance maximum is observed. However, there appears a prominent additional SERS resonance having comparable amplitude and shifted towards lower energies. It is also can be concluded from Fig. 3 that the value of the energy shift of the additional SERS resonance is definitely dependent on the distance $d_{ins}$ between the two metal layers in the studied structure.

To describe the obtained dependence of the energy red-shift of the additional SERS resonance
Fig. 2. (a) SERS spectra measured for a mono-molecular analyte layer (4 - ABT) on the surface of a standard SERS substrate. The spectra were measured at four different laser wavelengths, 488 nm, 532 nm, 568 nm and 647 nm, and with the same photoexcitation power density. (b) Raman spectra measured under identical experimental conditions from a modified SERS substrate with the buried thick silver layer below the top SERS-active silver layers; the two layers are separated by a 50 nm-thick dielectric slab.

on the distance $d_{ins}$, it is necessary to recall the theoretical calculation results for the spectrum of plasmon-polariton modes in layered structures [15]. Despite the fact that the upper metal layer is granular as required for the realization of the SERS enhancement, the planar localization of the surface plasma modes exceeds significantly the dielectric slab thickness. This justifies using for them the physical picture of the propagating thin film modes along with the corresponding theoretical considerations and results.

Figure 4 shows spectra of plasmon-polariton excitations in two different structures: the one containing a single metallic layer [Fig. 4(a)], and the other having two metallic layers, one
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Fig. 3. Spectral dependencies of the normalized SERS enhancement factor measured for the reference structure (a), as well as for three structures with an additional metal layer separated from the upper SERS layer by an insulator with the thickness $d_{ins} = 30$ nm (b), 50 nm (c) and 100 nm (d).

being infinitely thick, separated by an dielectric slab of thickness $d_{ins}$ [Fig. 4(b)]. As for the present consideration we’re interested in the lower-energy excitations only, the upper bulk-like plasma mode starting from $\omega_p$ at $k = 0$ and having a positive dispersion is not shown. In the first case there exist two plasmon-polariton modes, both exhibiting a linear dispersion in the $k \approx 0$ region corresponding to the speed of light $c$. The situation changes appreciably in the case of two metallic layers: the third plasmon-polariton mode with a linear dispersion appears, yet, its $k \approx 0$ group velocity $c_1$ is much lower that $c$ and essentially dependent on the geometric parameters of the structure. The appearance of this additional slow plasmon-polariton mode in the MIM structure explains the formation of the new SERS resonance. Moreover, the estimation of the energy shift dependence of this resonance on the distance $d_{ins}$ becomes feasible. Indeed, it is known that the scattering event takes place at scattered momentum values corresponding to the characteristic inverse size of the silver granules ($k \approx 1/\lambda$). For small momentum values, when a fundamental plasma mode has a group velocity approaching the speed of light, this condition ensures a SERS resonance at a frequency $\omega_2 \approx c/\lambda$. The additional SERS resonance related to the emergent slow plasmon-polariton mode will be observed at a lower frequency $\omega_1 \approx c_1/\lambda$. Therefore, the energy shift of the additional SERS resonance ($\Delta E$) is proportional to the difference in the group velocities ($c - c_1$) which is dependent on structure parameters. The group velocity of the slow plasmon mode in the limit $k \ll k_p$ is defined by the expression [15]:

$$c_1 = c[1 - (\lambda_p/2d_{ins})(1 + \coth(d_m/\lambda_p))]$$  \hspace{1cm} (1)

where $d_m$ is the thickness of the metallic SERS layer, $k_p = \omega_p/c$ is the plasma momentum, $\lambda_p$...
Fig. 4. Spectra of plasmon-polariton excitations in two different structures: containing a 
single metallic layer (a), and containing a metallic layer separated from the infinitely thick 
metallic layer by a dielectric slab with the thickness \( d_{\text{ins}} \) (b). The upper bulk-like plasma 
mode starting from \( \omega_p \) at \( k = 0 \) with a positive dispersion is not shown.

\[ \lambda_p = \frac{2\pi}{k_p} = \frac{2\pi c}{\omega_p} \]

\( \omega_p \) is the plasma frequency in metal \((\hbar \omega_p \sim 10 \text{ eV})\) [25]. This yields

\[ \Delta E \sim \frac{(c - c_1)}{a} \sim \frac{1}{d_{\text{ins}}} \]  \( \text{(2)} \)

Hence, the energy shift of the additional SERS resonance should be inversely proportional to 
the distance between the two metallic layers. Figure 5 presents the dependence of the measured 
energy shift of the additional SERS resonance on an inverse distance \( d_{\text{ins}} \). It is seen that for 
small values of parameter \( 1/d_{\text{ins}} \) the dependence is close to linear, which is in a full 
agreement with the above theoretical estimation (2). The deviation of the experimental dependence from 
the linear one at large values of parameter \( 1/d_{\text{ins}} \) is naturally expected since the expressions above 
corresponded to a small-value parameter expansion in \( 1/d_{\text{ins}} \).

The remarkable feature of the discovered subsidiary SERS resonance is its unexpectedly high 
intensity that is practically equal to the intensity of the main resonance. Moreover, the two
Fig. 5. Dependence of the measured energy shift of the additional SERS resonance on the inverse distance $d_{\text{ins}}$.

Resonance widths in Figs. 3(b)-3(d) are similar also, despite a greatly increased damping of the slow plasma mode compared with the fast ones, by an order of magnitude and even more [17]. The latter observation can be partially explained by the inhomogeneous broadening of the resonance by the fast mode in Fig. 3a due to the variations in both the dimensions of Ag granules and distances between them which affect the local plasma frequency. The fast mode resonance in Fig. 3a has a FWHM 2-3 times larger that is reported for the surface plasmon-polariton resonance on a bulk Ag [26]. Qualitatively it means that the peak Raman enhancement due to the fast mode is reduced by the same factor compared to the idealized situation when all granules are identical and display the local plasma resonances at the same frequency. Further quantitative explanation of the results requires sophisticated theoretical efforts and goes beyond the scope of the presented experimental work. It is also worth noting that additional plasmon-polariton modes appear in multilayer structures as a result of antiphase oscillations that are extremely difficult to excite by an incident light, in contrast to in-phase oscillations [27]. The presence of the near-field SERS mechanism for the excitation of plasmon-polariton modes leads to the comparable intensities of the main and additional resonances, which makes the presented experimental findings not only fundamentally interesting and important but also very promising for practical applications.

4. Conclusions

In this paper we demonstrated that specific MIM SERS substrates, engineered to have two metallic layers separated by a dielectric layer of a certain thickness, support a plasmon-polariton mode with a decreased group velocity and enable its effective optical excitation. The slow plasmon-polariton mode is revealed by an additional SERS resonance with a red-shifted energy and comparable amplitude along with the main plasmon-polariton SERS resonance occurring in the 450 - 550 nm wavelength range. It was confirmed that the energy of the novel resonance is determined by the thickness of the dielectric interlayer. The proposed engineering approach allows tuning the spectral position of the additional resonance over a fairly wide energy range.
and therefore presents a prominent interest for SERS applications.

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References

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24. The actual surface plasmon resonance energy for a silver-air interface corresponds to ~3.5 eV and differs considerably from the theoretical value of \( \omega_p/\sqrt{2} \) displayed in Fig. 4. It is explained by the screening effects from the bound electrons in the Ag material, which also soften the energies of both discussed MIM plasma modes.