Local enhanced site in surface enhanced infrared absorption with gold nano particle array by Rigorous coupled-wave analysis

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Keywords: Surface enhanced infrared absorption, Au particle array, RCWA, square column model

Abstract

Surface enhanced infrared absorption (SEIRA) is a phenomenon by which infrared absorption of molecules adsorbed onto metal evaporated films is greatly enhanced. To clarify the enhancement mechanism in the evaporated films, we simulated the distribution of the enhancement field between Au nano-square columns by rigorous coupled wave analysis (RCWA). No maximum enhancement was observed on the particle surface. This result demonstrates that the first layer effect is not dominant for the increase in this system of columns. Furthermore, the enhanced field oscillates periodically between the particles. This periodic oscillation is not plasmon behavior seen in the visible region. Results indicate the existence of enhancement mechanisms other than plasmons and indicate the possibility that the interference effect enhances infrared absorption.

1. Introduction

SEIRA is a phenomenon by which the infrared absorption of a molecule adsorbed onto a substrate having nanosized metal particles is greatly enhanced [1, 2]. The enhancement mechanism has not been elucidated. For SEIRA technology development, elucidating the enhancement mechanism is extremely important. Earlier work conducted in our laboratory has shown that the infrared absorption signal of molecules attached to evaporated Ag thin films is enhanced between Ag islands (Gap) [3]. To explain the experimentally obtained result, a square column model (SCM) was proposed [4, 5]. In this model, the electric field is concentrated in the gap based on the continuity of the electric displacement vector in the normal direction of the interface. Therefore, gaps play an important role in SEIRA. It is noteworthy that SCM does not incorporate consideration of the electric field distribution in the gap.

In recent years, studies have been undertaken to tune enhancement using special structures such as nanoantennas and nano-resonators [6–11]. The nanoantenna has a shape with length of several thousand nanometers and width of several hundred nanometers, with gaps arranged at intervals of several hundred nanometers. Those simulations revealed that when an electromagnetic wave is radiated on the nano-antenna, an augmented field is created in the gap between the adjacent nano-antennas [9]. Simulations of nano-resonators having a split-ring shape with parameters of 200 nm radius, 30 nm thickness, 80 nm width, and a 30 nm gap have revealed an enhanced field generated in the gap [11]. In both cases, the enhanced field in the gap is attributable to plasmon excitation. However, SEIRA was discovered in evaporated metal films. Many subsequent experimental measurements have also used evaporated metal films. The evaporated film structure and the shape of the nanoantenna (and nano-resonator) are significantly different. Moreover, no evidence indicates that the nanoantenna enhancement mechanism is applicable to the evaporated film. To clarify this point, this study used rigorous coupled wave analysis (RCWA) simulation to investigate the electric field distribution around a metal square column array having shape approximating that of an evaporated metal film [12]. By elucidating the electric field distribution in the gap, we can ascertain the origin of the SEIRA enhancement mechanism.
2. Calculation

2.1 RCWA

Simulation for this study used RCWA, which reproduced experimentally obtained results for fabricated Au square column arrays well in an earlier study [13]. A three-layer system consisting of the vacuum layer, a Au square column pattern with a model molecule layer, and a Si substrate layer was adopted for simulations. The square column array length and height were 50 nm and 6 nm, respectively. Also, 20 nm gaps separated the square columns. The wavenumber range of calculation was 1900–1500 cm$^{-1}$. The spectral resolution was 4 cm$^{-1}$. The incident light for TM mode was set at an incident angle of 5°. The Lorentz oscillator model, formulated as shown below, was adopted as the model molecule.

$$\varepsilon(\omega) = \varepsilon_{\text{inf}} + \frac{f}{(\omega_0^2 - \omega^2) + i\gamma\omega}$$  \hspace{1cm} (1)

Therein, $\varepsilon_{\text{inf}} = 2.08$, $f = 2.8 \times 10^{27}$ s$^{-2}$, $\gamma = 8.0 \times 10^{12}$ s$^{-1}$, and $\omega_0 = 3.216 \times 10^{14}$ s$^{-1}$.

The model molecule height was fixed at the square column height (6 nm). For calculation, S4 free software was used [14]. The dielectric constants of the substrate (Si) and metal particles (Au) were referred from values reported in the literature [15, 16].

2.2 The pattern layer setting

Two pattern layers were set for calculations.

First, to clarify the rough electric field distribution in the gap, the gap was divided into three parts. Model molecules were placed in each part (figure 1). The X part is a gap in the direction of the incident electric field. Actually, SCM relies on the assumption that the electric field increases in this part. The Y part is a gap perpendicular to the incident electric field. The Diagonal part is the part that is not blocked by particles.

Next, to clarify the fine electric field distribution, each part of figure 1 was allowed 1 nm width. The electric field intensity distribution is calculated by changing the divided region in which the model molecules are arranged. Figure 2 presents an example in which the X part is divided: (a) is a division method for calculating the electric field intensity distribution perpendicular to the particle interface; (b) is for the tangential distribution.

3. Result and discussion

The SCM model is based on electric field enhancement considering the continuity of electric displacement $D$. Therefore, enhancement in the Y part and Diagonal part are not considered. To verify it using RCWA, we divide the region into three parts and calculate the absorbance.

Figure 3 portrays the infrared absorption spectrum corresponding to the carbonyl stretch region of polyacrylic acid on a Au array substrate. The X part sandwiched by the square column interface perpendicular to the direction of the incident electric field showed great enhancement. When the enhancement factors were calculated by performing volume correction of the model molecules, the enhancement factors were, respectively, about 20 for the X part, about 9 for the Diagonal part, and about 1.5 for the Y part. The simulation result by which the absorption increases in the gap in the direction of the incident electric field is consistent with the SCM hypothesis. Enhancement of the Y part sandwiched by the interface parallel to the electric field direction was not strong. No enhancement occurred, probably because of the absence of particles in the direction of the electric field, which is consistent with the SCM assumption. The Diagonal part showed intermediate enhancement between the X part and Y part. This finding is discussed later.

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Figure 1. Schematic drawing of divided unit cell. The double-headed arrow indicates the direction of the incident electric field.
As described above, enhancement using metal particles with special structures such as nano-antennas is attributable to plasmons. Plasmons excited at the interface decay exponentially in intensity along with distance from the interface. Therefore, we simulate the normal electric field distributions respectively in the X part and Y part. The results are presented in Figure 4.

The vertical axis shows the absorbance, which is normalized by the maximum value of the absorption intensity. The horizontal axis shows the position from the interface: 0 is nearest the interface; 10 is at approximately the center of the gap. No maximum enhancement was found nearest the interface. This result supports the experimentally obtained results verifying the surface first layer effect using self-assembled monolayer and showing a lack of effect [17]. Furthermore, the enhanced field in the normal direction changes periodically. The enhanced field in the square column array is concentrated mainly in the X part; the Y part has a much weaker field. These findings support the SCM assumption.

Periodic change in the electric field strength can result from the interference effect of the incident wave. Actually, SCM relies on the assumption that the electric field concentrates in the gap. The electric field distribution is not considered. The interference effect is consistent with this assumption. In other words, the interference effect is probably included in SCM.

Even in the X part, the electric field distribution is not plasmon-like. In the visible light region, it was confirmed that the Au fine particle system excites plasmons. The distribution of the normal direction enhanced field in the X part in the visible light region was simulated using RCWA, as was the distribution of enhanced field

![Figure 2. The schematics of arrangement of model molecules to simulate electric field distribution. (a) normal distribution and (b) tangential distribution (example X part). Only one quarter of the unit cell is shown for symmetry.](image)

![Figure 3. The IR absorption spectrum of model molecule. Black line represents the X part, green line represents the Diagonal part, red line represents the Y part, respectively.](image)
in the infrared region. The normal electric field distribution of X part in the visible region was simulated to ascertain whether the plasmon distribution appeared. To excite plasmons, the structural parameters of the pattern layer were set to 5 nm particle size, a 20 nm particle gap, and 5 nm particle height. Modified values for the Lorentz oscillator model parameters of the model molecules were assumed to be a mixture of polymethyl methacrylate and rhodamine 6G \[18\]. The following parameters were used:

\[
\varepsilon_{\infty} = 2.320, \quad f = 7.42 \times 10^{17}[s^{-2}],
\]

\[
\omega_0 = 3.55 \times 10^{15}[s^{-1}], \quad \gamma = 1.0 \times 10^{12}[s^{-1}].
\]

The wavenumber range of calculation was 15000–22000 cm\(^{-1}\); the spectral resolution was 100 cm\(^{-1}\).

The simulation result, presented in figure 5, shows the greatest enhancement at the particle interface, with rapid decay away from the interface. This behavior is the plasmon behavior itself, with plasmon enhancement in the visible region. This simulation illustrates the plasmon effect. In other words, results confirmed that if the plasmon effect is sufficient, it can be simulated by RCWA. Therefore, it can be inferred that absorption enhancement in the infrared region is not attributable to plasmons.

Next, to clarify all electric field distributions in the gap, the electric field distribution of the tangential component is simulated in addition to the normal component. Results are presented in figure 6: zero denotes the center of the square side, 25 denotes the particle edge, and 26–35 denote the Diagonal part. In figure 6(a), the absorbance distribution in the X part apparently shows no

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**Figure 4.** The normal distribution of absorbance. (a) X part and (b) Y part.

**Figure 5.** The normal distribution of absorbance in the visible region.
significant change. Absorbance in the Diagonal part weakens gradually with distance from the X part. Furthermore, as shown in figure 6(b), absorbance in the Y part increases slightly as it approaches the particle edge. The points above underscore the possibility that a large enhancement field in the X part has penetrated the Diagonal part and the Y part.

In contrast to the visible region, no plasmon contribution was observed in the infrared region. To confirm the plasmon effect, the peak position of the absorption band was simulated with spectral resolution of 1 cm$^{-1}$, as shown in figure 7.

The peak position is shifted to a considerable degree near the particle interface. Then, as the distance from the interface increases, the shift decreases sharply. This behavior is similar to that of the electric field intensity distribution in the visible region. The peak position might have shifted because of band distortion caused by Fano resonance. Consequently, it is possible that plasmons were excited and that they caused a peak shift. However, plasmons do not contribute to absorption enhancement.

Finally, 3D mapping of the absorbance from the calculation results above is displayed in figure 8.
Enhancement occurs between particles in the direction of the electric field. It varies periodically, but shows maximum enhancement at a distance from the interface. As this figure shows, the enhancement field penetrates from the gaps (X part).

4. Conclusions

To verify the distribution of the enhancement field in the evaporated film, RCWA simulations were conducted using a square column array. No maximum electric field enhancement was observed near the particle interface. This finding supports the experimentally obtained results. Therefore, SEIRA in the evaporated film probably has no physical surface first layer effect. Furthermore, results demonstrated that marked enhancement occurs between particles in the direction of the electric field. These simulation results are consistent with the SCM assumption. It is noteworthy that the enhancement field in the normal direction for particles has a periodic distribution. This behavior differs considerably from that of plasmons. The difference is clear, even when compared to simulation conducted in the visible region. However, as the absorption peak is shifted, plasmons might be excited. In other words, plasmons are excited in SEIRA, but they do not contribute to absorption enhancement. The electric field changes periodically between particles. Therefore, we presume that absorption enhancement results from interference effects.

Acknowledgments

This work was supported financially by Grantin-Aid for Scientific Research, JSPS KAKENHI Grant numbers 16H03820 and 18H01998.

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