Computer simulation of key structural parameters for enhanced infrared absorption with Au nano-array

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Abstract
The optical constants of thin films with nanoscale structures, such as metamaterials and nanostructured films used in surface enhanced infrared absorption (SEIRA), are represented by effective medium approximation (EMA). In a representative EMA, the effective permittivity is determined by parameters such as the volume filling factor \( F \). In a metal square column array modeled on an evaporated film, the effective permittivity is determined by the gap size/particle size ratio \( f \). However, \( f \) is also expressed as a function of \( F \). For this study, we simulated the SEIRA spectrum using a model in which \( f \) and \( F \) were varied independently to investigate which was the most important parameter in the square column array. The results showed all the simulations performed, results showed that the gap size/particle size ratio \( f \) is an important parameter for the increase in SEIRA in the square column array. This study has led to new discoveries that support elucidation of the SEIRA enhancement mechanism.

1. Introduction
The phenomenon of dramatically increasing infrared absorption of molecules adsorbed to metal nanoparticles is called surface-enhanced infrared absorption (SEIRA) [1, 2]. Use this phenomenon is expected to improve the sensitivity of infrared spectroscopy. Evaporated metal films have been used widely for SEIRA substrates. Nevertheless, research in recent years has been conducted on using artificial structures for metal nanoparticles to generate stronger enhancement fields and adjusting resonance with molecular vibrations [3–8]. This artificial structure is called a metamaterial. The macroscopic optical constants of thin films with nanostructures smaller than the wavelength, such as metamaterials and substrates used to enhanced infrared absorption, are described by effective medium approximation (EMA). The Maxwell–Garnett model [9] and the Bruggeman model [10] are representative EMAs. In both models, for example, in the case of a two-phase system in which metals are dispersed in a dielectric matrix, the effective permittivity is found based on three parameters: the permittivity of the matrix, the permittivity of the metal, and the volume filling factor \( F \) of the metal. Furthermore, the SEIRA phenomenon is known to be reproducible using these models [11–15].

After proposing the Square Columnar Model (SCM) [16] to elucidate the phenomenon of increased infrared absorption, we used electron beam lithography to create a Au square column array to demonstrate the validity of SCM [17]. Furthermore, results confirmed that the experimentally obtained values and the values calculated by SCM can be reproduced using rigorous coupled wave analysis (RCWA) simulation [18, 19]. In SCM, because the effective dielectric function \( \varepsilon_{\text{eff}} \) of the composite film was simply estimated as a series capacitor, the gap size/particle size ratio \( f \) is the key parameter, as shown in figure 1 and equation (1).

For normal incidence, from Maxwell’s equations,
\[
\varepsilon_{\text{p}} E_{\text{p}} = \varepsilon_{\text{d}} E_{\text{d}} = \varepsilon_{\text{eff}} E_{\text{eff}},
\]
where \( \varepsilon_{\text{eff}} = \varepsilon_{\text{p}} \left( \frac{1 + f}{\eta + f} \right), \quad f = \frac{g}{p} \) and \( \eta = \varepsilon_{\text{d}} / \varepsilon_{\text{p}} \).
However, in a square column array, $F$ is a function of $f$ as shown in equation (2) below.

$$F = \frac{p^2 \times h}{(p + g)^2 \times h} = \frac{p^2}{p^2 + 2pg + g^2} = \frac{\frac{p^2}{g^2}}{\frac{p^2}{g^2} + \frac{2pg}{g^2} + \frac{g^2}{g^2}}$$

where

$$f = \frac{g}{p}$$

$$= \left(\frac{1}{f}\right)^2 \left(\frac{1}{f^2} + \frac{2}{f} + 1\right) = \left(\frac{1}{f}\right)^2 \times f^2 = \frac{1}{1 + 2f + f^2} = \frac{1}{(f + 1)^2}$$

In those equations, $F$, volume filling factor; $p$, particle size; $g$, gap size; $h$, particle height; $f$, gap size/particle size ratio.

That is, it remains unclear which of $F$ and $f$ is the key parameter. Alternatively, $f$ might just be a variation of expression of $F$. To clarify this, it is necessary to change $F$ and $f$ independently. However, in a square column array, changing $f$ by changing one or both of the gap size and particle size invariably changes $F$ as well. Therefore, as shown in figure 2, this difficulty is verified using models of two types that change $F$ and $f$ independently. First, a model was used in which the square column was rotated without changing the unit cell size ((p + g)²) or the square column size ($F$ fixed). This is designated as the Rotate Column (RC) model. $F$ is determined by the unit cell size and the square column size, but when the square column is rotated, the minimum gap changes without changing the unit cell size or the square column size (figure 2).

Additionally, contrary to the RC model, simulation is performed by fixing $f$ and changing only $F$. As shown in figure 3(b), the square column size and the gap (gap_x) size in the direction of the incident electric field ($E_x$) are fixed. Actually, only gap_y is changed. In this case, $F$ changes as the unit cell size changes. However, because the size of gap_x is fixed, $f$ in the direction of the incident electric field does not change. For verification, as shown in figure 3(c), simulation is also performed when gap_y is fixed and only gap_x is changed. This is designated as the Change only the gap in one direction (COGOD) model. Using these models, we clarify which of $F$ and $f$ is the key parameter using RCWA simulation.

2. Calculation

Rigorous coupled wave analysis (RCWA), which was used for the simulations conducted for this study, is a method supporting evaluation of the electromagnetic field in the periodic structure. Results of RCWA simulations using the Au square column array show good agreement with measurements of evaporated film and the Au square column array [19, 20]. Therefore, this simulation method is adopted. A three-layer system consisting of the vacuum layer, a Au square column pattern with a model molecular layer, and a Si substrate layer was adopted for simulations. The applicable sizes of the SEIRA phenomenon investigated using various particle sizes and gap sizes are reported [21]. According to this results, the particle size and the gap size were determined as follows. The height of the square column array was constant at 30 nm. The initial values of square column array length and the distance between the arrays were, respectively, 250 nm and 100 nm. In the RC model, the
The size of the unit cell is set to 350 nm. The Au square column is rotated to perform the simulations. The range is 0°—45°. For the COGOD model, the simulations were conducted by changing only gap_x or only gap_y. The range is 5 nm to 100 nm. The wavenumber range of calculation was 1900–1500 cm⁻¹. The spectral resolution was 4 cm⁻¹. The incident light in TM mode was set to 0°. The Lorentz oscillator model, formulated as shown below, was adopted as the model molecule.

**Figure 2.** Schematic diagram of the Rotate Column model, where the volume filling factor F is fixed and the gap size/particle size ratio f is changed.

**Figure 3.** Schematic diagram of change only the gap in one direction model, where the gap size/particle size ratio, f is fixed and volume filling factor, and F is changed: (a) square column array with equal gap_x and gap_y; (b) model diagram that fixes gap_x and changes only gap_y; and (c) model diagram that fixes gap_y and changes only gap_x.
Therein, $\varepsilon_{\text{inf}} = 2.08$, $f = 2.8 \times 10^{27} \text{ s}^{-2}$, $\gamma = 8.0 \times 10^{12} \text{ s}^{-1}$, and $\omega_0 = 3.216 \times 10^{14} \text{ s}^{-1}$.

In the case of the Rotate Column model, the model molecules were placed across the gap in the Au square column. In the case of the COGOD model, they were placed between the particles in the direction of the incident electric field ($E_x$). The model molecule height was set as equal to the square column height. For calculation, S4 free software was used [22]. The dielectric constants of the substrate (Si) and metal particles (Au) were referred from values reported in the literature [23, 24].

3. Results and discussion

3.1. RC model

The typical simulation results are presented in figure 4.

As the figure illustrates, as the angle of the metal square column changes, the absorption increases as the rotation angle increases. Next, a plot of the enhancement factor obtained from the angle of the metal square column and the obtained absorption intensity is shown (figure 5). The enhancement factors were calculated by dividing the absorbance of infrared spectra on the Au square column array by that directly on the bare silicon substrate (without the Au square column arrays).

This figure shows an increasing tendency of the enhancement factor of the infrared absorption from around 26°. In this simulation, the volume filling factor ($F$) is constant. The gap size between particles and particle size changed locally. Results therefore confirmed that the enhancement effect depends on the gap size to particle size ratio. Furthermore, the enhancement factor does not change so much up to 25°, probably because the gap size is not so small when the metal square column is rotated at a low angle. Simultaneously with the minimum gap changes, a region with a wide gap appears. However, as described in an earlier report [12], change in the enhancement factor of infrared absorption is remarkable in the region where the gap size is small. For that reason, the change in the minimum gap contributes greatly.

3.2. COGOD model

The calculation result obtained from the COGOD model is presented in figure 6.

Figure 6(a) presents the absorption intensity shown for the gap size/particle size ratio when gap_y is fixed and gap_x is changed. The absorption intensity was normalized by the model molecule amount. In this case, $F$ changes with GPR, but the absorption intensity shows almost identical GPR dependence as that of an earlier experiment [12] and the calculation result [14]. Figure 6(b) shows the calculated absorption intensity results as a
function of gap_y when gap_x is fixed. Actually, $F$ changes with the change of gap_y, although no marked change in absorption intensity is apparent. Our earlier reported results \cite{15} confirm that the enhancement fields created within the gaps are not confined within it, but rather seep out of it. The decrease in gap_y means that the relative distance of gap_x, where the field is generated, is getting closer, and that small gap_y will be affected by the field seeping out from adjacent gap_x. In figure 6(b), the slight increase in absorption intensity with the decrease of gap_y indicates that the effect of the field seeping out from adjacent gap_x appears.

When $F$ is fixed and $f$ is changed, the absorption intensity depends on $f$. Even when $f$ is fixed and $F$ is changed, the absorption intensity depends on $f$. Moreover, even when both $F$ and $f$ are changed, the absorption intensity is almost dependent on $f$. These results in the range of the scale investigated in this paper confirmed that the key structural parameter in infrared absorption enhancement using a Au nano-array is $f$: the gap size/particle size ratio.

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**Figure 5.** Enhancement factor as a function of rotation angles.

**Figure 6.** (a) Normalized absorption intensity as a function of the gap size/particle size ratio (GPR). (b) Absorption intensity for changes in gap_y.
4. Summary

We investigated whether the important parameters that determine the effective permittivity in a square metal square column array are the volume filling factor \( F \) or the gap size/particle size ratio \( f \). The SEIRA absorption spectra were simulated by RCWA using models in which \( F \) and \( f \) were changed independently. Results of a simulation using a model that fixes \( F \) and changes only \( f \) by rotating a metal square column (RC model), and a simulation using a model that fixes \( f \) and changes only \( F \) (COGOD model) show that the absorbance intensity was strongly \( f \)-dependent in both models. Therefore, results in the range of the scale investigated in this paper confirmed that the key structural parameter in infrared absorption enhancement using a Au nano-array is \( f \); the gap size/particle size ratio. This finding might be a new step towards elucidating SEIRA enhancement mechanisms.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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