

Studies on Photothermal Conversion by Noble Metal Nanoparticles

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Chapter 1

Introduction

1.1 Background

Local plasmon resonance in noble metal nanoparticles (NPs) has long been known as an optical absorption band in the visible region [1]. This optical absorption is attributed to the collective motion of conduction electrons in the NPs induced by an applied electromagnetic field [2, 3]. Since the local field enhancement arising from the local plasmon resonance was proved to be useful for sensors in the late 20th century [4–7], it has been extensively studied for its potential applications, such as surface-enhanced Raman spectroscopy (SERS) [4–11], biosensing [12], photocatalysis [13], and localized light sources [14].

The thermoplasmonic effect [15], which also arises from local plasmon resonance, has been considered a side effect of the electromagnetic field enhancement. In recent years, interest in this photothermal conversion effect of noble metal NPs has grown rapidly because of its potential use as a heat source at the micro- or nanometer scale [16–20]. The advantages of this photothermal conversion include a fast conversion response on the order of picoseconds [19] and the fact that electrical connections are unnecessary, in contrast to conventional metal wire Joule heaters. There are mainly two types of noble metal NP heaters: a colloidal solution [16, 20–24] and a two-dimensional array [25–29]. A noble metal NP colloid is often used as a mobile nano heat source for applications in cancer therapy [16, 21], photoacoustic imaging [16, 22, 23], and vapor generation [20, 24]. On the other hand, applications of two-dimensional arrays of noble metal NPs include planar photoacoustic emission [25] and microfluidic manipulation

[26–29]. Their advantage is spatially well-defined heat generation. When used in combination with spatial arrangement of metal NPs, two-dimensional arrays are expected to develop a complex temperature gradient at the micro- or nanometer scale. However, two issues limit their practical use: low photothermal conversion efficiency and high fabrication cost. The photothermal conversion efficiency is determined mainly by their optical absorption properties. To obtain high optical absorption, considerable effort has been devoted to studying the size and shape dependence of the optical absorption of two-dimensional metal NP arrays [30, 31]. However, their optical absorption is limited to several tens of percent, even at their local plasmon resonant frequency [31, 32]. In addition, well-designed two-dimensional metal NP arrays are often prepared by e-beam lithography of metal thin films, which is not suitable for large-area fabrication because of the high cost.

A noble metal NP/dielectric shape control layer (SCL)/dielectric phase control layer (PCL)/silver mirror multilayered thin film, namely, a local plasmon resonator (Fig. 1.1 [10]), was self-assembled using the dynamic oblique deposition (DOD) technique [33–38]. In this structure, the SCL determines the shape of the NP array on top of it, and the PCL controls the optical path length within the thin film. The structure basically acts as an optical cavity [39], which enables it to exhibit wide tunability of its optical absorption from ~ 0 to more than 0.99 depending on the PCL thickness and incident light wavelength [10]. This high optical absorption of the local plasmon resonator has been used to demonstrate highly enhanced SERS spectra [10].

The unique optical properties of local plasmon resonators make them attractive for use as photothermal conversion heaters. Because of their high optical absorption, they are expected to realize high-efficiency photothermal conversion. In addition, patterning of the smooth PCL layer enables them to make regions with high optical absorption of ~ 1 and low optical absorption of ~ 0 without the need to pattern the metal NPs. Therefore, if the generated heat is transferred to the ambient fluid efficiently, they are useful as a spatiotemporally controllable microheater.

In this thesis, a comprehensive study of the photothermal conversion properties of local plasmon resonators is presented. The four main objectives of this thesis are summarized as follows: (i) evaluating the optical absorption properties of local plasmon resonators, (ii) obtaining

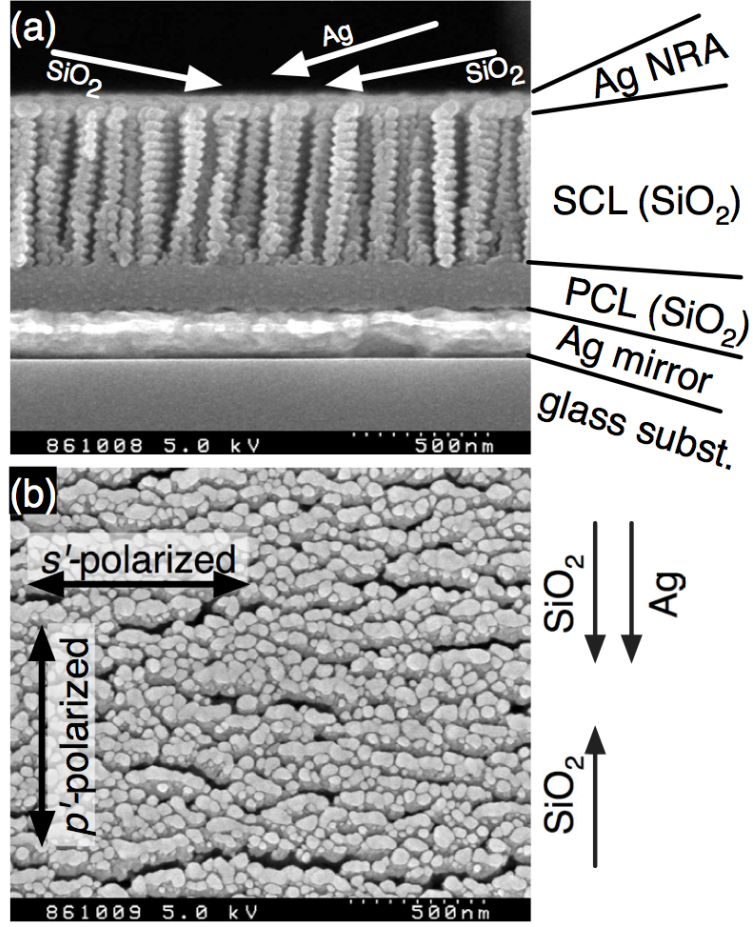


Figure 1.1: Scanning electron microscopy images of (a) cross section and (b) surface of Ag nanorod array (NRA)/SCL/PCL/Ag mirror structure [10].

spatial controllability of photothermal conversion, (iii) obtaining temporal controllability of photothermal conversion by the photoacoustic effect, and (iv) demonstrating photothermally induced microfluidic control as one of the applications.

1.2 Outline of This Thesis

Chapter 2 presents a theoretical investigation of the optical absorption properties of local plasmon resonators. Transfer matrix calculation methods are employed to yield the optical absorption spectra and Poynting vector of local plasmon resonators, which also reveal the depth profiles of the electric field and optical absorption coefficient.

Chapter 3 presents the detailed fabrication method of local plasmon resonators using the DOD technique. The fabricated samples are evaluated by scanning electron microscopy and optical measurements.

Chapter 4 presents an investigation of the spatial controllability of the photothermal conversion of local plasmon resonators. The heat generation under continuous laser irradiation is evaluated experimentally and theoretically using samples with a wide range of optical absorption.

Chapter 5 presents investigations of the temporal controllability of the photothermal conversion of local plasmon resonators using the photoacoustic effect, which is sensitive to changes in the sample surface temperature. More efficient photoacoustic emission from local plasmon resonators than from bulk absorbing materials is demonstrated to show their advantages for temporal temperature modulation. Then, a one-dimensional heat transfer model is introduced to evaluate the effect of the thermal conductivity of thin films on efficient photoacoustic emission. In addition, approaches to enhance the photoacoustic emission from local plasmon resonators by reducing the thermal conductivity are proposed.

Chapter 6 presents microfluidic manipulation as one of the applications of photothermal conversion in local plasmon resonators. It is demonstrated that the photothermally induced Marangoni flow is controlled by spatiotemporally controlled photothermal conversion at the micrometer scale, which is useful for mixing, ranging, collecting, and sorting microparticles.

Chapter 7 summarizes the major conclusions of this study and offers suggestions for future works.

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Chapter 2

Optical Absorption Properties of Local Plasmon Resonators

2.1 Introduction

Evaluation of optical absorption properties is essential in understanding the performance of photothermal conversion heaters. In general, photothermal conversion efficiency of a sample is estimated by its total optical absorption [1–4]. However, because the generated heat has to transfer from the sample to the surrounding fluid, the depth profile of the optical absorption, i.e., that of the heat generation is of great interest [5]. If the light absorption layer is thick or deep inside the sample, the temperature change of the sample surface is small, which results in the small variation of the fluid temperature. In particular, the effect of the depth profile of the optical absorption becomes prominent when the photothermal conversion heater is operated at high frequency [5, 6]. For such an application, optical absorption localized at sample surface is optimal [6].

The local plasmon resonators have noble metal NPs/dielectric/Ag mirror structures that act as an optical cavity. Because of strong interference, their optical absorption is tunable from ~ 0 to more than 0.99 in the visible–near infrared (NIR) region [7]. These values represent the total optical absorption, which includes the optical absorption of all layers in the local plasmon resonator. So far, however, the optical absorption of each layer has not been addressed. The

local plasmon resonators contain two layers that possess high extinction coefficients: the noble metal NP layer and the Ag mirror layer. It is important to elucidate the contribution of these layers to photothermal conversion in order to analyze and control the local temperature at the micrometer scale.

In this chapter, the optical absorption properties of local plasmon resonators are theoretically evaluated using transfer matrix and energy balance calculations. A generalized optical absorption calculation method for a multilayered thin film with isotropic layers is provided here and applied as an optical model of the local plasmon resonator. From the calculation results, the effect of the layer thicknesses, depth profile of the electric field, and depth profile of the optical absorption coefficient are evaluated in order to discuss the suitability of the local plasmon resonator as a photothermal heater.

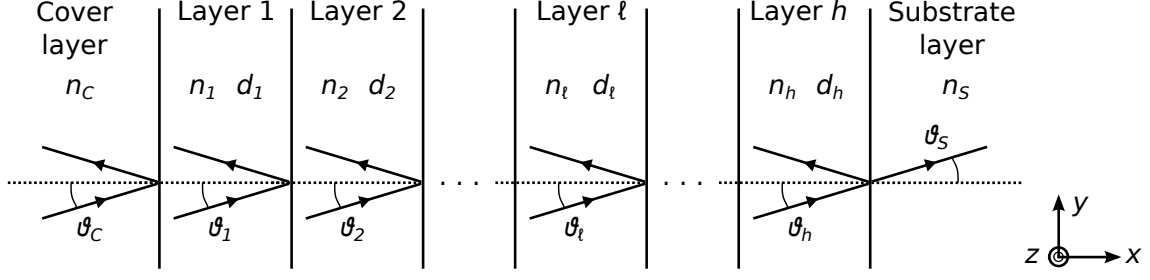


Figure 2.1: Optical model of a multilayered thin film.

2.2 Optical Absorption Calculation

2.2.1 Governing Equation

The formalism for the propagation of light in optical media has long been discussed [8]. The optical properties of a multilayered thin film are known to be described well by a transfer matrix method, which is usually utilized to design the optical reflectance and transmittance of an optical coating. By using this method, the electromagnetic field distribution within the thin film can be derived. When this method is combined with energy flow description using the Poynting vector, the depth profile of the optical absorption per unit depth is also obtainable. The following is a brief description of the calculation method for those optical properties of a multilayered thin film with isotropic layers.

Figure 2.1 shows the optical model, which consists of a cover layer, multiple thin layers ($l = 1, 2, \dots, h$), and a substrate layer. The x axis is taken to be normal to the layer surface, and the y and z axes are parallel to the surface. The thickness of each layer is d_l , the refractive index is n_l , and the angle of the incident light is θ_l , where the subscript identifies the layer. From Snell's law,

$$n_C \sin \theta_C = n_1 \sin \theta_1 = \dots = n_l \sin \theta_l = \dots = n_h \sin \theta_h = n_S \sin \theta_S. \quad (2.1)$$

Four traveling wave fields exist in the layers: p-polarized light propagating forward (E_p^+ , H_p^+) and backward (E_p^- , H_p^-), and s-polarized light propagating forward (E_s^+ , H_s^+) and backward (E_s^- , H_s^-). The y and z components of these electromagnetic fields are obtainable from Fig. 2.2. The total in-plane electromagnetic field (E_y , H_z , E_z , H_y) in the medium is described by

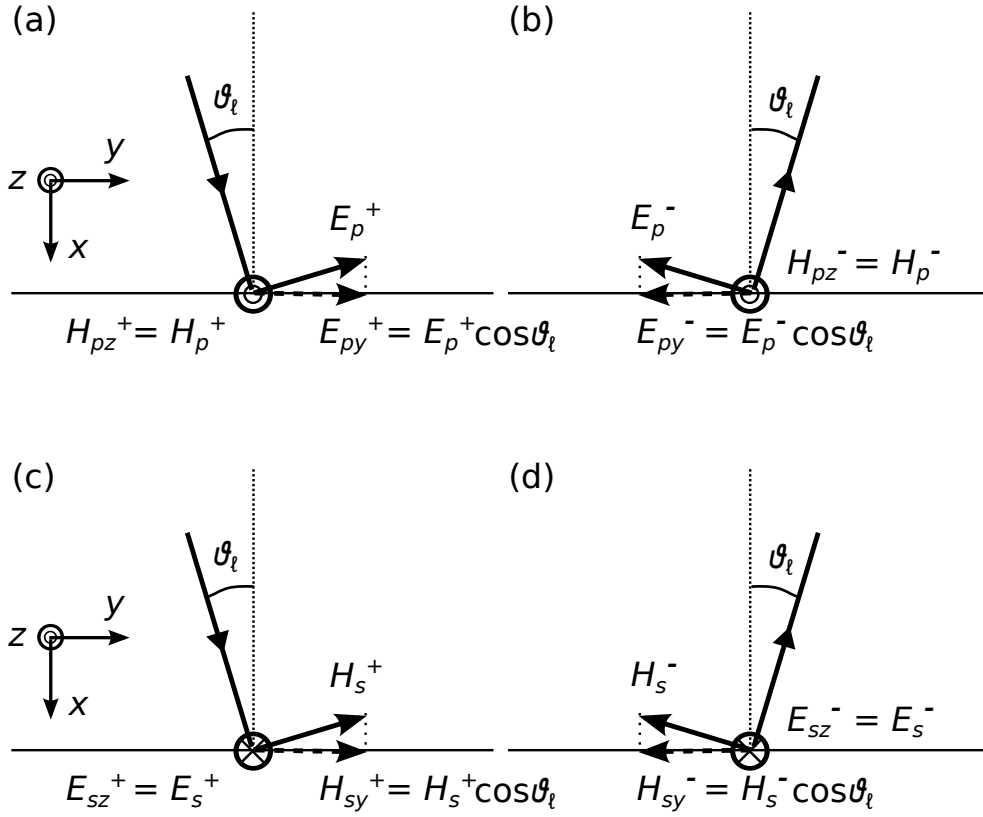


Figure 2.2: Electromagnetic field of p-polarized light propagating forward (a) and backward (b), and that of s-polarized light propagating forward (c) and backward (d). The incident plane is taken to be normal to the axis of z .

the sum of those components multiplied by the complex coefficients,

$$\hat{F}\vec{a} = \vec{m}, \quad (2.2)$$

where

$$\hat{F} = \begin{pmatrix} E_{py}^+ & E_{py}^- & E_{sy}^+ & E_{sy}^- \\ H_{pz}^+ & H_{pz}^- & H_{sz}^+ & H_{sz}^- \\ E_{pz}^+ & E_{pz}^- & E_{sz}^+ & E_{sz}^- \\ H_{py}^+ & H_{py}^- & H_{sy}^+ & H_{sy}^- \end{pmatrix}, \quad \vec{a} = \begin{pmatrix} a_p^+ \\ a_p^- \\ a_s^+ \\ a_s^- \end{pmatrix}, \quad \vec{m} = \begin{pmatrix} E_y \\ H_z \\ E_z \\ H_y \end{pmatrix}. \quad (2.3)$$

The matrix $\hat{F}$ is the *field matrix*, $\vec{a}$ is the *field coefficient*, and $\vec{m}$ is the *total field*. In an isotropic medium, the following relations hold:

$$\frac{H_z^+}{E_y^+} = -\frac{H_z^-}{E_y^-} = \frac{n}{z_0 \cos \theta} = \gamma_p, \quad \frac{H_y^+}{E_z^+} = -\frac{H_y^-}{E_z^-} = -\frac{n \cos \theta}{z_0} = \gamma_s, \quad (2.4)$$

where $z_0 = (\mu_0/\varepsilon_0)^{1/2}$ is the impedance of vacuum, μ_0 is the permeability of vacuum, and ε_0 is the permittivity of vacuum. Using Eqs. (2.4), Eqs. (2.3) can be modified as

$$\hat{F} = \begin{pmatrix} 1 & 1 & 0 & 0 \\ \gamma_p & -\gamma_p & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & \gamma_s & -\gamma_s \end{pmatrix}, \quad \vec{a} = \begin{pmatrix} a_p^+ \\ a_p^- \\ a_s^+ \\ a_s^- \end{pmatrix} = \begin{pmatrix} E_{py}^+ \\ E_{py}^- \\ E_{sz}^+ \\ E_{sz}^- \end{pmatrix}, \quad \vec{m} = \begin{pmatrix} E_y \\ H_z \\ E_z \\ H_y \end{pmatrix}. \quad (2.5)$$

The four traveling wave fields defined in Eqs. (2.5) change their phase linearly with displacement in the x direction. For a right-to-left displacement, from $x = x_0$ to $x = x_0 - d_l$, the phase change is given by the *phase matrix*

$$\hat{A}_{dl} = \begin{pmatrix} e^{+i\phi_l} & 0 & 0 & 0 \\ 0 & e^{-i\phi_l} & 0 & 0 \\ 0 & 0 & e^{+i\phi_l} & 0 \\ 0 & 0 & 0 & e^{-i\phi_l} \end{pmatrix}, \quad (2.6)$$

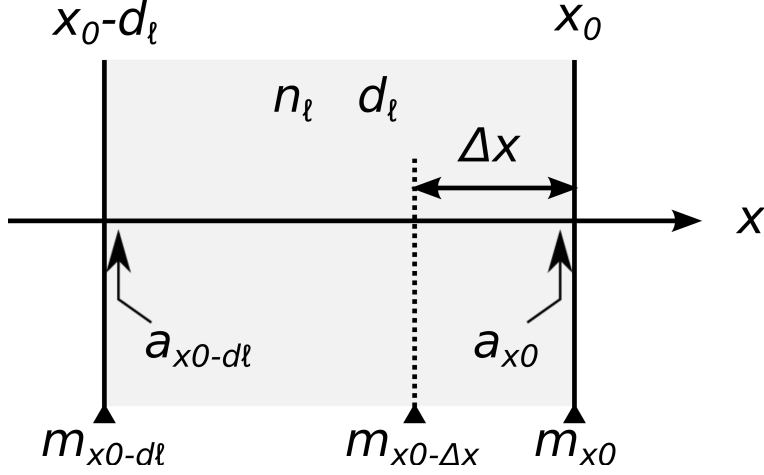


Figure 2.3: Field coefficient and total field in layer l .

where

$$\phi_l = k_0 n_l d_l \cos \theta_l. \quad (2.7)$$

The value of k_0 is the magnitude of the *wave vector* $\vec{k}_0$, which is $2\pi/\lambda_0$, where λ_0 is the wavelength of the incident light in vacuum. The phase matrix represents the phase change of the field coefficient in layer l :

$$\vec{a}_{x_0-d_l} = \hat{A}_{dl} \vec{a}_{x_0}. \quad (2.8)$$

Please note that these vectors, $\vec{a}_{x_0-d_l}$ and $\vec{a}_{x_0}$, represent the field coefficient within layer l (Fig. 2.3). From Eqs. (2.2) and (2.8), the total fields at the positions $x = x_0$ and $x = x_0 - d_l$ are related by

$$\vec{m}_{x_0-d_l} = \hat{F}_l \hat{A}_{dl} \hat{F}_l^{-1} \vec{m}_{x_0} = \hat{M}_l \vec{m}_{x_0}. \quad (2.9)$$

The matrix $\hat{M}_l$ is called the *characteristic matrix* of layer l . Because the total field $\vec{m}$ is conserved on either side of the layer boundary, the total field at the cover, $\vec{m}_C$, and that at the substrate, $\vec{m}_S$, can be related by

$$\vec{m}_C = \hat{M}_1 \hat{M}_2 \cdots \hat{M}_h \vec{m}_S = \hat{M} \vec{m}_S. \quad (2.10)$$

This equation denotes the transformation of the total field by the multilayered thin film system.

The characteristic matrix of each layer, $\hat{M}_l$, can be derived from Eqs. (2.5)–(2.7):

$$\hat{M}_l = \hat{F}_l \hat{A}_{dl} \hat{F}_l^{-1} = \begin{pmatrix} \hat{M}_{lp} & \cdot \\ \cdot & \hat{M}_{ls} \end{pmatrix}, \quad (2.11)$$

where

$$\hat{M}_{lp} = \begin{pmatrix} \cos \phi_l & i\gamma_{pl}^{-1} \sin \phi_l \\ i\gamma_{pl} \sin \phi_l & \cos \phi_l \end{pmatrix}, \quad \hat{M}_{ls} = \begin{pmatrix} \cos \phi_l & i\gamma_{sl}^{-1} \sin \phi_l \\ i\gamma_{sl} \sin \phi_l & \cos \phi_l \end{pmatrix}. \quad (2.12)$$

Therefore, the matrix $\hat{M} = \hat{M}_1 \hat{M}_2 \cdots \hat{M}_h$ can be determined from incident light wavelength and the refractive index n_l , thickness d_l , and incident light angle θ_l of each layer in the entire system.

The reflectance and transmittance of the entire system can be derived as follows: from Eqs. (2.2), (2.5), and (2.10),

$$\hat{F}_C \vec{a}_C = \hat{M} \hat{F}_S \vec{a}_S, \quad (2.13)$$

where

$$\vec{a}_C = \begin{pmatrix} E_{pyC}^+ \\ E_{pyC}^- \\ E_{szC}^+ \\ E_{szC}^- \end{pmatrix}, \quad \vec{a}_S = \begin{pmatrix} E_{pyS}^+ \\ 0 \\ E_{szS}^+ \\ 0 \end{pmatrix}. \quad (2.14)$$

The values of E_{pyC}^+ and E_{szC}^+ are the y and z components of the electric field of the incident light, respectively. Note that there is no electric wave propagating backward in the substrate layer. Equation (2.13) determines the other parameters, E_{pyC}^- , E_{szC}^- , E_{pyS}^+ , and E_{szS}^+ , in Eqs. (2.14). Then, the reflectance R and transmittance T are given by

$$R_p = |r_p|^2 = \left| \frac{E_{pyC}^-}{E_{pyC}^+} \right|^2, \quad T_p = |t_p|^2 = \left| \frac{E_{pyS}^+}{E_{pyC}^+} \right|^2 \quad (\text{for p-polarized light,}) \quad (2.15)$$

$$R_s = |r_s|^2 = \left| \frac{E_{szC}^-}{E_{szC}^+} \right|^2, \quad T_s = |t_s|^2 = \left| \frac{E_{szS}^+}{E_{szC}^+} \right|^2 \quad (\text{for s-polarized light,}) \quad (2.16)$$

where r_s , r_p , t_p , and t_s are the Fresnel coefficients.

The electric field at an arbitrary position x is obtainable using the characteristic matrix.

Figure 2.3 illustrates the position $x = x_0 - \Delta x$. By using the refractive index n_l , incident light angle θ_l , and thickness $d_l - \Delta x$, the characteristic matrix for the layer between $x = x_0 - d_l$ and $x = x_0 - \Delta x$, i.e., $\hat{M}_{dl-\Delta x}$, is derived. Therefore, the total field at the position $x = x_0 - \Delta x$ is obtained from

$$\vec{m}_{x_0-\Delta x} = \hat{M}_{dl-\Delta x}^{-1} \vec{m}_{x_0-dl} = \hat{M}_{dl-\Delta x}^{-1} \hat{M}_{l-1}^{-1} \cdots \hat{M}_1^{-1} \vec{m}_C, \quad (2.17)$$

where the matrices $\hat{M}_1, \dots, \hat{M}_{l-1}$ are already derived and the vector $\vec{m}_C$ is determined by Eqs. (2.2), (2.5), and (2.14). The square of the electric field strength at an arbitrary position is then given by

$$|E|^2 = |E_y|^2 + |E_z|^2, \quad (2.18)$$

using the total field vector $\vec{m}$.

The depth profile of the optical absorption can be evaluated using the Poynting vector p_x , which represents the energy flux along the x axis and is given by

$$p_x = \frac{1}{2} \text{Re}\{E_y H_z^* - E_z H_y^*\}. \quad (2.19)$$

The in-plane electromagnetic fields at position x , E_y , H_y , E_z , and H_z , are obtained as the total field $\vec{m}$. By differentiating p_x with respect to x and dividing it by the total incident energy I_0 , the optical absorption per unit length, α_{eff} , can be obtained:

$$\alpha_{eff}(x) = -\frac{1}{I_0} \frac{\partial p_x(x)}{\partial x}. \quad (2.20)$$

We call α_{eff} the “effective absorption coefficient” because its integration over the x axis gives the total absorption A of the sample.

2.2.2 Optical Model for Local Plasmon Resonators

In order to evaluate the optical absorption properties of the local plasmon resonators using the transfer matrix method, their structures and optical properties are described by using a simple model (Fig. 2.4). Figures 2.4(a) and 2.4(b) show the typical scanning electron microscopy (SEM) images of the local plasmon resonator, which consists of Au NP/SiO₂ SCL/

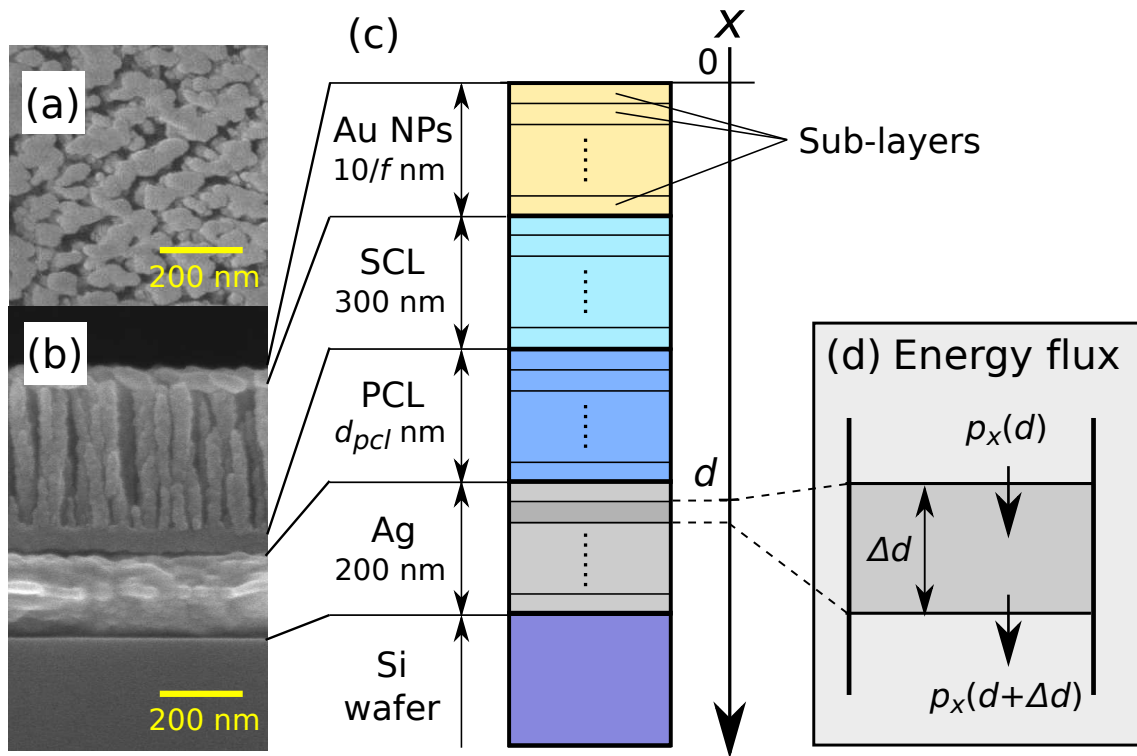


Figure 2.4: Modeling of local plasmon resonators whose structures are shown in the SEM images ((a) surface morphology and (b) cross section). They are described by (c) multilayered homogeneous structures that have Au NP/SCL/PCL/Ag layers. Each layer is divided into sublayers in order to calculate optical absorption distribution. Figure (d) shows energy balance within a single sublayer.

SiO₂ PCL/Ag mirror layer whose fabrication method is introduced in Chapter 3. Because the dimensions of the nanostructures in the in-plane direction in the layers are much smaller than the wavelengths in the visible or NIR wavelength regions, we treated our thin films as homogeneous multilayers (Fig. 2.4(c)). The thicknesses of the layers have been defined in Fig. 2.4(c) and the thicknesses of SCL, PCL, and Ag layers are determined from the SEM images. Since we vary the PCL thicknesses in the model, we represent their values by d_{pcl} . For the Au NP layer, Au is deposited to an average thickness of 10 nm. Because the Au NP layer forms an island structure, its geometrical thickness is defined as $10/f$ nm where f is the volume fraction of Au. The refractive index of each layer is defined as follows. The Au NP layer is treated as an effective medium of a mixture of a metal nano-sphere and a transparent material having the same dielectric constant as the SCL. The effective dielectric function is evaluated by the Maxwell-Garnett model [8] as;

$$\epsilon^{av} = \epsilon_{scl} \frac{(1 + 2f) \epsilon + 2(1 - f) \epsilon_{scl}}{(1 - f) \epsilon + (2 + f) \epsilon_{scl}}. \quad (2.21)$$

Here, f is the volume fraction of the nano-spheres, ϵ is the dielectric function of the metal, and ϵ_{scl} is the in-plane dielectric function of the SCL, which will be defined later. From the SEM observations, f is estimated to be $0.5 \leq f \leq 1$. The dielectric function of the metal, ϵ , for the incident photon energy ω , is represented by the Drude model:

$$\epsilon = \epsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\delta)}, \quad (2.22)$$

where ω_p is the plasma frequency, ϵ_{∞} is the dielectric constant at high frequencies, and δ is the reciprocal of the scattering time. The bulk values of $\omega_p = 8.96$ eV, $\epsilon_{\infty} = 7.44$ are standard values [9, 10], and δ is used as the fitting parameter, because corresponding value for nanostructures could be larger compared to the bulk value. For the SCL, we assumed in-plane refractive index $\sqrt{\epsilon_{scl}} = n_{scl}$ for normal incident light. Because the packing density of an SCL is small, its in-plane refractive index is estimated to be smaller than that of the bulk SiO₂, so that $1 \leq n_{scl} \leq 1.47$. The PCL consists of SiO₂ that has a refractive index of $n_{pcl} = 1.47$. The refractive index of the Ag mirror layer is reported in literature [11].

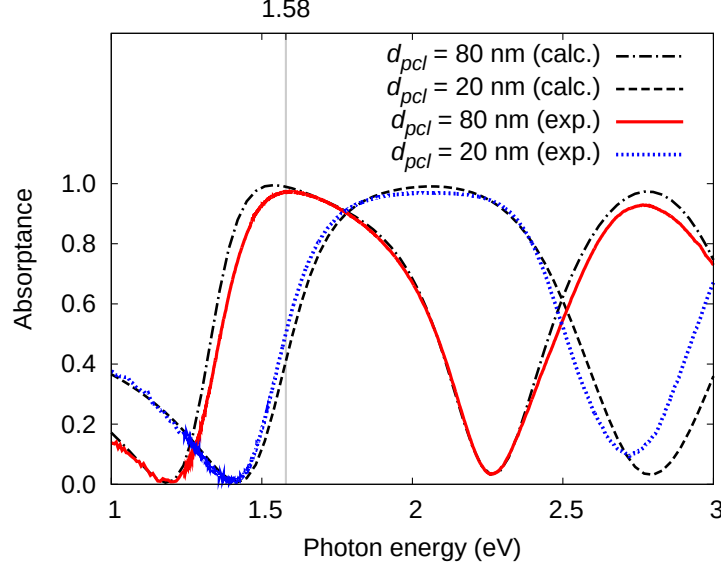


Figure 2.5: Calculated and measured optical absorption spectra of local plasmon resonators with $d_{pcl} = 20$ and 80 nm.

2.2.3 Parameter Determination

The optical absorption spectra were calculated *via* a transfer matrix formalism [8] described in Section 2.2.1 at normal incidence with unpolarized light and fitted to the experimental results using fitting parameters f , δ , and n_{scl} (Fig. 2.5). Because the optical transmittance and scattering of our samples are negligibly small, the optical absorption A is evaluated as $A = 1 - R$, where R is the optical reflectance. The value of n_{scl} determines the cycle of the periodic undulation observed in the optical absorption spectra, which arises from interference. Thus, n_{scl} was chosen to fit the peak positions of the undulation of the calculated spectra to the positions of the measured spectra. On the other hand, the peak shape and intensity are sensitive to both δ and f of the Au NP layer. Therefore, n_{scl} , δ , and f were chosen to reproduce the intensity and shape of the absorption peaks. Figure 2.5 shows the fitting results, which agree well with experimental results when $\delta = 1.8$, $f = 0.75$, and $n_{scl} = 1.25$. The fitting results of f and n_{scl} are consistent with the SEM images. The value of δ is significantly larger than the bulk value, because the scattering probability increases as a result of the defects and surface roughness of NPs. The calculation results agrees well with the experimental results for both the values of d_{pcl} , i.e., 20 and 80 nm. Because this model reflects the optical characteristics of our samples quite well, we utilized it to discuss the detailed optical absorption properties of

the local plasmon resonators.

2.2.4 Derivation of Optical Absorption Depth Profile

To numerically obtain the optical absorption per unit depth (Eq. (2.20)), each layer of the model structure was divided into thin sublayers of thickness Δd (Fig. 2.4(c)). The optical absorption for each sublayer was calculated using the Poynting vector p_x , which represents the energy flux along the x axis and is given by Eq. (2.19). Regarding the sublayer at the position $x = d$ (Fig. 2.4(d)), the effective absorption coefficient, α_{eff} , can be obtained as follows:

$$\alpha_{eff}(d) = \frac{p_x(d) - p_x(d + \Delta d)}{\Delta d I_0}, \quad (2.23)$$

where I_0 is the intensity of the incident light.

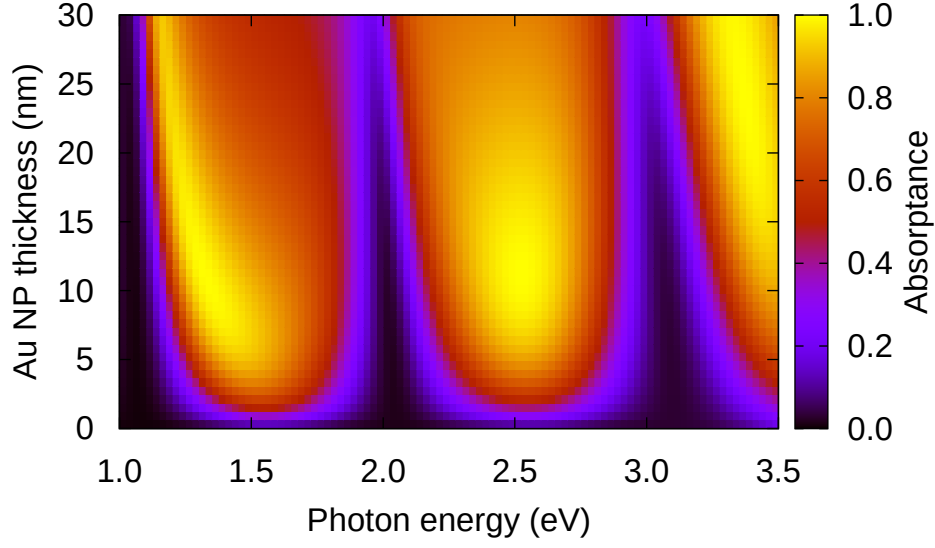


Figure 2.6: Calculated optical absorption spectra of local plasmon resonators with various Au NP thicknesses. The PCL thickness is fixed at 120 nm.

2.3 Results and Discussion

2.3.1 Effect of the Layer Thickness

The optical absorption spectra of local plasmon resonators with various PCL and Au NP thicknesses were calculated using the optical model obtained in the previous section. Because the targeted wavelength region for the use of their photothermal conversion is in the visible–NIR region, their optical absorption properties at around 1.0–3.5 eV are discussed in this section.

Figure 2.6 shows the calculated optical absorption spectra of local plasmon resonators with various average Au NP thicknesses of 0–30 nm. The PCL thickness is fixed at 120 nm. The yellow portion represents high optical absorption. At photon energies of around 1.3, 2.5, and 3.3 eV, the calculated spectra has optical absorption peaks. The peak position does not change significantly as a function of the Au NP thickness. The thickness determines the magnitude of the absorption peaks, and the optimal Au NP thickness to achieve high optical absorption at 1.0–3.0 eV is around 8–12 nm.

Figure 2.7 shows the calculated optical absorption spectra for local plasmon resonators with various PCL thicknesses of 0–250 nm. The average Au NP thickness is fixed at 10 nm. The

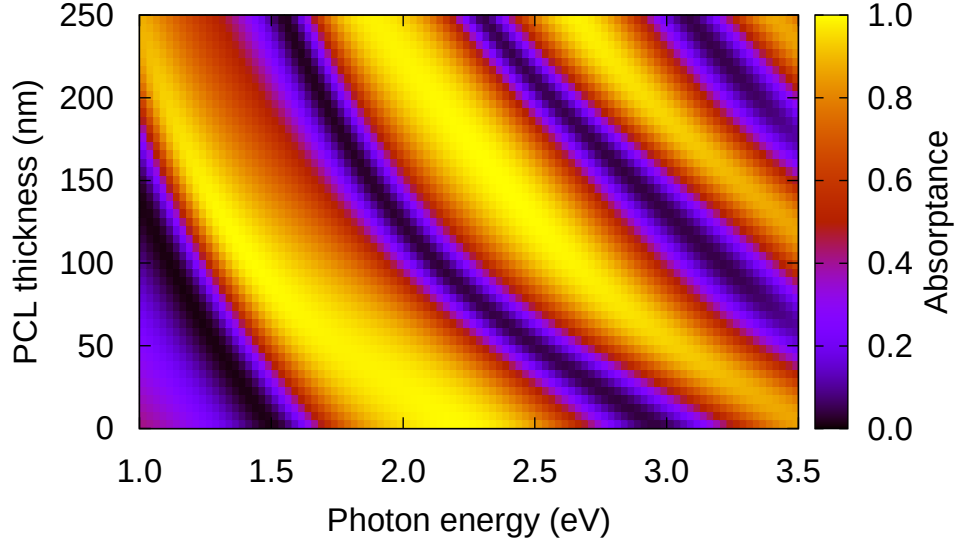


Figure 2.7: Calculated optical absorption spectra of local plasmon resonators with various PCL thicknesses. The average Au NP thickness is fixed at 10 nm.

Table 2.1: Calculated total optical absorption and optical absorption for each layer of local plasmon resonators with $d_{pcl} = 20, 80,$ and 250 nm at a wavelength of 785 nm. Average Au NP thickness is fixed at 10 nm.

d_{pcl} (nm)	Total absorption	Absorption for each layer			
	A	Au NPs	SCL	PCL	Ag
20	0.404	0.339	0.000	0.000	0.005
80	0.993	0.990	0.000	0.000	0.003
250	0.012	0.008	0.000	0.000	0.004

yellow portion represents high optical absorption. The optical absorption varies periodically as functions of the photon energy and PCL thickness, which indicates the effect of interference. The calculation result suggests that varying the PCL thickness from 0 to 250 nm is sufficient to obtain local plasmon resonators with various optical absorption values at a certain photon energy. For example, at a wavelength of 785 nm (1.58 eV), the calculated optical absorption varies significantly from 0.01 at a PCL thickness of 250 nm to 0.99 at a PCL thickness of 80 nm (Table 2.1). The depth profiles of the electric field and optical absorption coefficients are evaluated by fixing the Au NP thickness at 10 nm and incident light wavelength at 785 nm.

2.3.2 Depth Profile of the Electric Field

Figure 2.8 shows $|E|^2$ defined in Eq. (2.18) as a function of the position from the surface of local plasmon resonators with PCL thicknesses of 80 and 250 nm at a wavelength of 785 nm. The average Au NP thickness is fixed at 10 nm. When $d_{pcl} = 80$ nm (Fig. 2.8(a), $A = 0.99$), a standing wave exists between the Au NP layer and the Ag mirror layer, and $|E|^2$ in the air layer is almost unity. This result indicates that once the light is incident on the structure, it will stay within the cavity and be absorbed by the structure [7]. On the other hand, when $d_{pcl} = 250$ nm (Fig. 2.8(b), $A = 0.01$), strong standing waves exist in the air layer as well as in the cavity. The node of the standing wave is matched to the Au NP layer. Because there is no electric field vibration around the Au NP layer, it is expected to absorb little light energy.

2.3.3 Depth Profile of the Optical Absorption

Figure 2.9(a) shows the calculated effective absorption coefficient of a highly absorptive local plasmon resonator ($A = 0.99$) at a wavelength of 785 nm (1.58 eV) as a function of the position from the surface. The thicknesses of the Au NP and PCL layers are fixed at 10 and 80 nm, respectively. The effective absorption coefficient of the Au NP layer is three orders of magnitude higher than that of the Ag mirror layer. Thus, the optical absorption of the local plasmon resonator is localized in the ~ 10 -nm-thick Au NP layer, which lies at the sample surface. For comparison, the effective absorption coefficient of a Si wafer ($A = 0.67$) is shown in Fig. 2.9(b). The effective absorption coefficient of the Si wafer is three orders of magnitude smaller than that of the Au NP layer in the local plasmon resonator. It decreases gradually over several micrometers (Fig. 2.9(b), inset). This result suggests that the Si wafer has an absorption layer that is several micrometers thick. Thus, local plasmon resonators realize highly localized light absorption compared to bulk absorbing materials.

For quantitative analysis, the optical absorption of each layer of the local plasmon resonators was calculated for samples with $d_{pcl} = 20, 80$, and 250 nm (Table 2.1). It is important to note that the calculated total absorption of these samples varies from ~ 0.01 to 0.99, which suggests that the photothermal conversion of local plasmon resonators can be spatially controlled through the patterning of d_{pcl} . Regardless of the variation in the total absorption, the

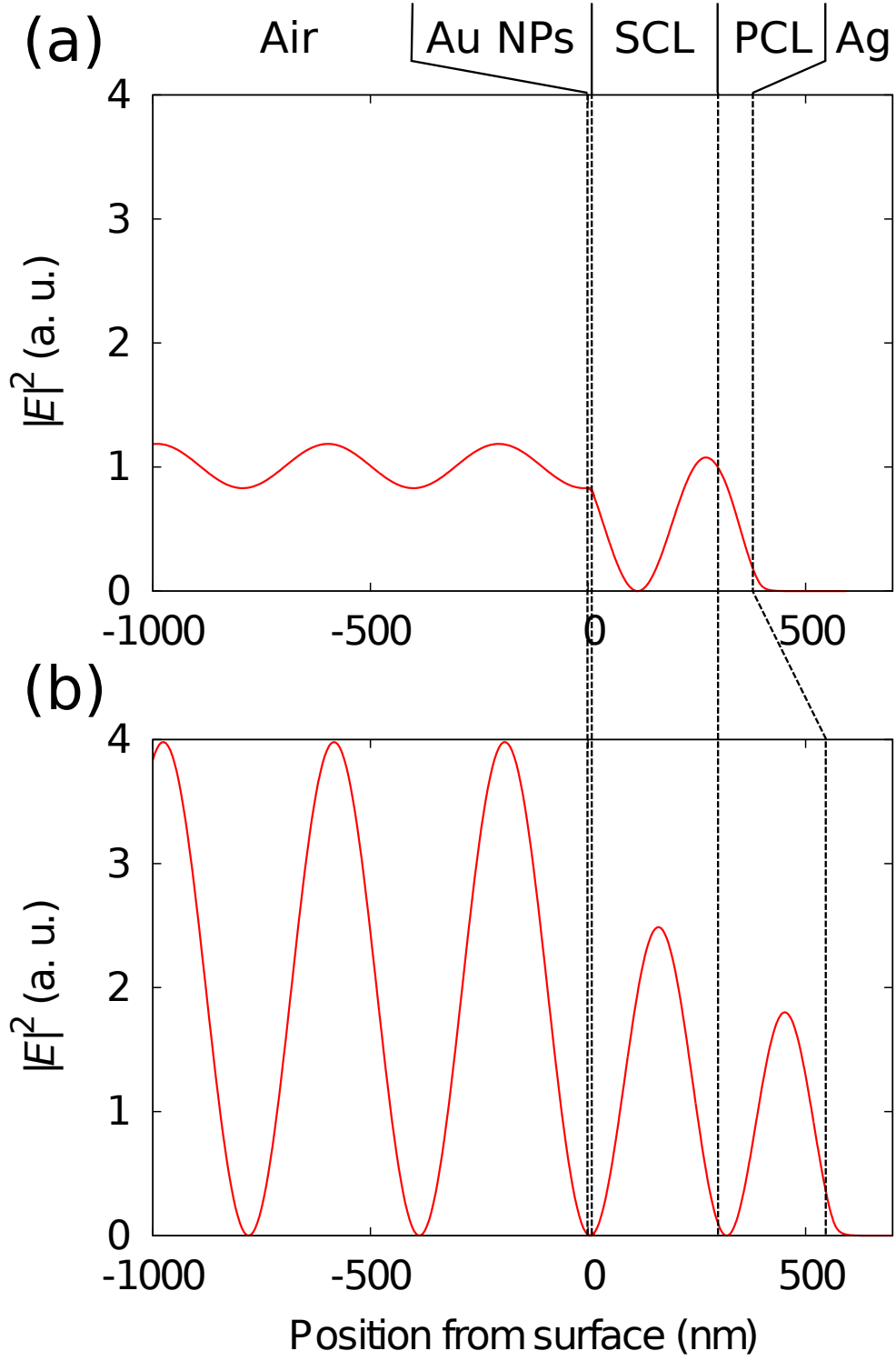


Figure 2.8: Value of $|E|^2$ as a function of position from the surface of local plasmon resonators with PCL thicknesses of (a) 80 nm ($A = 0.99$) and (b) 250 nm ($A = 0.01$).

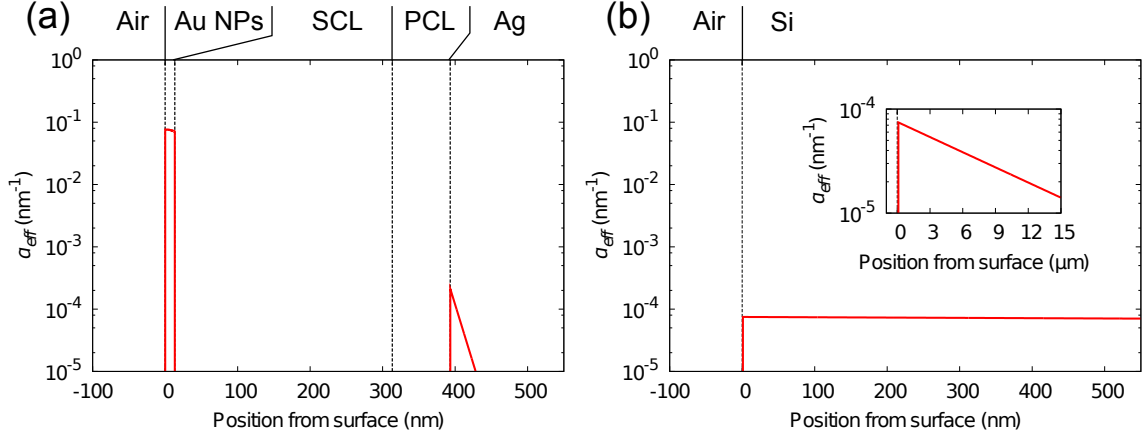


Figure 2.9: Effective absorption coefficient α_{eff} (nm⁻¹) as a function of position from surface for (a) local plasmon resonator with 80-nm-thick PCL ($A = 0.99$) and (b) Si wafer ($A = 0.67$) at a wavelength of 785 nm. Inset in (b) shows a gradual decrease in α_{eff} over several micrometers in the Si wafer.

absorption of the Ag mirror layer is negligibly small. In this calculation, up to 99.6% of the total absorption occurs in the Au NP layer when the total optical absorption is high ($A = 0.99$). This result suggests that local plasmon resonators can efficiently convert light energy to heat energy in the Au NP layer and can exhibit dramatic alterations in surface temperature.

2.4 Conclusion

In this chapter, the optical absorption properties of local plasmon resonators having Au NP/PCL/SCL/Ag mirror layers were investigated theoretically using transfer matrix and energy balance calculations.

The effect of variations in the layer thicknesses on the optical absorption spectra of the local plasmon resonators were evaluated using an optical model. By using the optimal Au NP thickness, which is around 10 nm, a high optical absorption of ~ 0.99 was achieved in the visible–NIR region. When the PCL thickness was modulated from 0 to 250 nm, one of the optical absorption peak moved from 2.2 to 1.0 eV, and the optical absorption at a single photon energy (1.58 eV) varied widely from 0.01 (at $d_{pcl} = 250$ nm) to 0.99 (at $d_{pcl} = 80$ nm). These results suggest that the optical absorption of local plasmon resonators is widely tunable by choosing the proper layer thicknesses and incident light wavelength.

The depth profile of the electric field was calculated for the optical model of local plasmon resonators with high optical absorption and high optical reflectance. Within the multilayered structure of the resonators, a standing wave exists because of interference, which assists either high optical absorption or high optical reflection. By using the Poynting vector derived from the electromagnetic field distribution, the depth profile of the optical absorption was evaluated. The optical absorption of local plasmon resonators is highly localized (more than 99%) in the Au NP layer (~ 10 nm), which is extremely thin compared to the optical absorbing layer of a bulk Si wafer (several micrometers). Therefore, their photothermal conversion is expected to be highly localized in the thin surface layer and to contribute to the rapid increase in the local temperature.

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Chapter 3

Fabrication of Local Plasmon Resonators

3.1 Introduction

This chapter is devoted to the fabrication method of local plasmon resonators: The local plasmon resonator is a multilayered thin film consisting of a Au NP layer, nanostructured dielectric layers, and a Ag mirror layer, which can be self-assembled by DOD technique [1].

DOD is a modified physical vapor deposition process [2–7], which is suitable for fabricating thin films consisting of nanocolumns over more than several hundreds of square millimeters. By controlling the substrate angle and in-plane rotation during the deposition of materials, two-dimensional arrays of helical, cylindrical, or zigzag columns are obtainable [8]. The applications of these columnar structures include variety of optical coatings with anisotropic magnetic and optical properties [2, 4] and sensors [9]. It was recently shown that those columns are also useful as a template to control the shape of NPs deposited on them [1, 10, 11].

A local plasmon resonator can be prepared by dividing the dielectric layer into two layers: a SiO₂ nanocolumn layer and a SiO₂ plane layer. The SiO₂ nanocolumn layer controls the shape of the NP array on top of it and is called the “shape control layer”. The SiO₂ plane layer controls the optical path length within the thin film and is called the “phase control layer”. By patterning the PCL thickness before the preparation of SCL and Au NPs, the samples with

different optical absorption can be spatially arranged.

In this chapter, the fundamentals of the DOD technique and the detailed fabrication method of the local plasmon resonator are presented. In addition, the fabricated samples are observed by SEM to evaluate the structures; their optical absorption spectra are also evaluated.

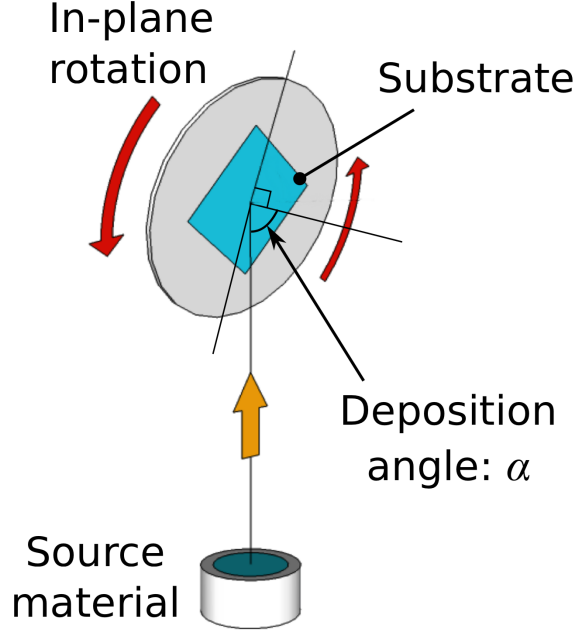


Figure 3.1: Schematic drawing of DOD.

3.2 Fundamentals of Dynamic Oblique Deposition

The DOD technique is an efficient method of fabricating discontinuous thin films with columnar structures and NP arrays [2–8]. The following is a brief introduction to the growth mechanism of those structures.

The essential feature of the DOD technique is the deposition angle α of the substrate measured from the surface normal (Fig. 3.1). When α is large enough, the growth of distinct columnar structures is observed; the growth mechanism is summarized in three steps as follows:

1. Nucleation [Fig. 3.2(a)]

In the early steps of physical vapor deposition, the adatoms absorbed on the sample surface form clusters on it or re-evaporate after diffusion. The clusters are unstable and continuously absorb and release adatoms. A cluster starts to grow when the number of adatoms in it exceeds a critical number, which is called nucleation.

2. Self-shadowing effect [Fig. 3.2(b)]

When the diffusion length of the adatoms is not very long, the self-shadowing effect restricts their diffusion area. Because deposition is oblique, a shadowed area is formed behind the islands of deposited material. Therefore, in the shadowed area, no new nucle-

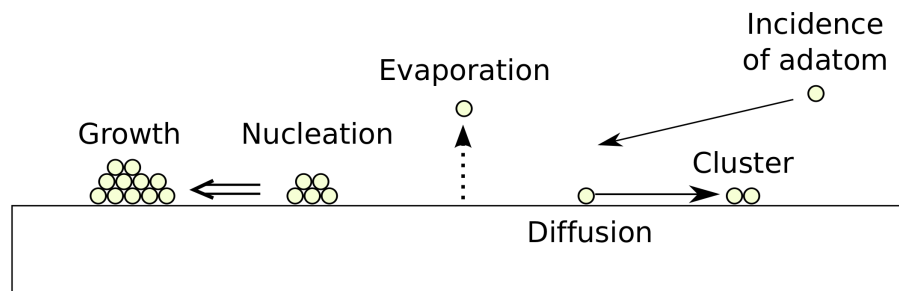
ation will occur, and non-continuous arrays of islands grow on the sample surface.

3. Growth of columns [Fig. 3.2(c)]

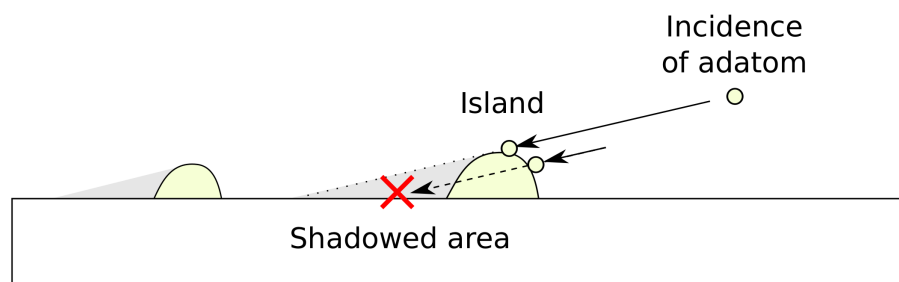
Because of the shadowing effect, the adatoms are absorbed by the top of the islands, which subsequently grow into columnar shapes. It is known experimentally that the angle of the formed columns, β , measured from the surface normal and the deposition angle α are related as $2 \tan \beta = \tan \alpha$.

The mechanism described above explains the method of fabricating an array of angled straight columns on a sample surface [5]. By controlling the substrate in-plane rotation as well as the deposition angle, various structures can be fabricated. For example, serial bideposition, in which the substrate is rotated 180° after each deposition of a certain amount, produces bundled zigzag structures with an elongated surface morphology (Fig. 3.3(a), [8]). Continuous in-plane rotation of the substrate during deposition results in helical or cylindrical structures (Fig. 3.3(b–d), [8]) with a pitch determined by the angular speed of the rotation.

(a)



(b)



(c)

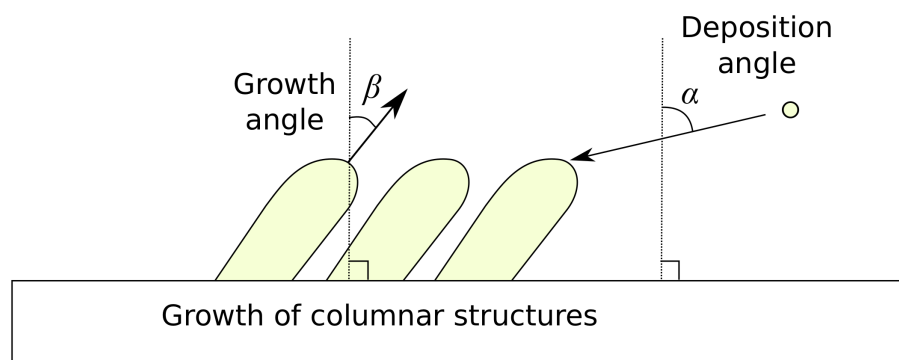


Figure 3.2: Schematic drawings of DOD mechanism: (a) nucleation, (b) self-shadowing effect, and (c) growth of columns.

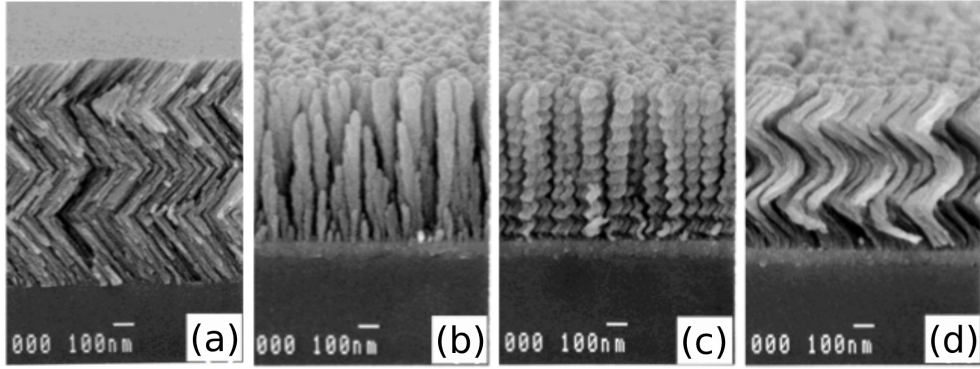


Figure 3.3: SEM images of nanocolumns fabricated by DOD. By controlling the deposition angle and in-plane rotation of the substrate, (a) zigzag structures, (b) cylinders, and (c,d) helices with various pitches are prepared [12].

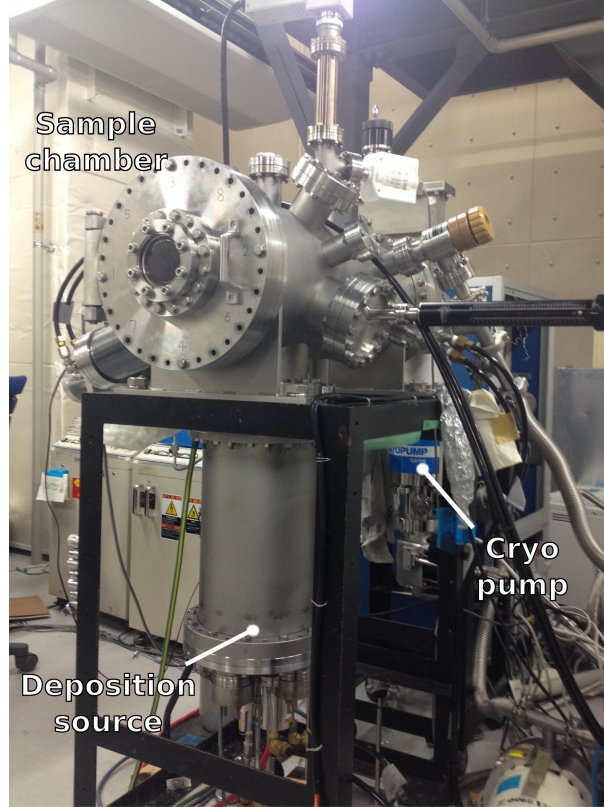


Figure 3.4: DOD apparatus.

3.3 Experiments

Local plasmon resonators with Au NP/SiO₂ nanocolumn/SiO₂/Ag mirror multilayered structures were fabricated using a DOD apparatus (Fig. 3.4) on either a glass or a Si substrate ~ 50 mm² in size [1]. Before sample preparation, the substrate was cleaned in an acetone ultrasonic bath for 10 min and subsequently blown dry using compressed air. It was then placed in a UV ozone cleaner (UV253S, Filgen) for 30 min. The cleaned substrate was attached to the substrate holder, whose in-plane rotation and deposition angle are controllable by a stepping motor using the LabVIEW program. The deposition chamber is equipped with a cryopump, which evacuates the chamber to as low as 1×10^{-4} Pa before deposition. Targets of Au (purity 99.99%), SiO₂ (purity 99.99%), and Ag (purity 99.99%) were evaporated separately from electron beam sources at a distance of 480 mm from the substrate. The thickness of the thin film deposited on the substrate was monitored by a quartz crystal deposition monitor (XMT/2, INFICON), which was set near the substrate.

The fabrication conditions of each layer of the local plasmon resonators are listed in Table

Table 3.1: Conditions of sample preparation, where α represents the deposition angle.

	Thickness (nm)	α ($^\circ$)	In-plane rotation (rpm)	Deposition rate (nm s $^{-1}$)
Au NP array	0.6–8.6	83.4	0	0.1–0.2
SCL (SiO $_2$)	400	78.6	20	0.1–0.2
PCL (SiO $_2$)	0–220	0	0	0.1–0.2
Ag mirror	200	0	0	0.5–0.8

3.1. First, a smooth Ag layer 200 nm in thickness was deposited on the substrate from the surface normal direction. The pressure during Ag deposition was $\sim 1 \times 10^{-3}$ Pa, and the vapor flux of Ag was 0.5–0.8 nm s $^{-1}$. Onto this Ag mirror, a PCL of SiO $_2$ was deposited from the surface normal direction. The thickness of the PCL was varied from 0 to 220 nm to obtain samples with various optical absorption properties (see Chapter 2). This series of different SiO $_2$ thicknesses was realized on a single substrate by moving a shutter incrementally across the sample during SiO $_2$ deposition. On the PCL, an SCL of SiO $_2$ was prepared; this layer was evaporated until it reached a thickness of 400 nm. During SCL deposition, the deposition angle (measured as the angle from the normal) was fixed at 78.6 $^\circ$, and the substrate was rotated continuously and rapidly at a speed of 20 rpm. The pressure during SiO $_2$ deposition was $\sim 5 \times 10^{-4}$ Pa, and the vapor flux of SiO $_2$ was 0.1–0.2 nm s $^{-1}$. A Au NP layer, the average thickness of which was varied from 0.6 to 8.6 nm, was deposited at a deposition angle of 83.4 $^\circ$ onto the SCL.

Optical reflection measurements at an angle of incidence of 2 $^\circ$ were made using single-beam spectrophotometers (USB4000/Ocean Optics and DTS-1700/Polychromix) in the wavelength range of 300 nm $< \lambda < 1700$ nm. Because the optical transmittance and scattering of the samples are negligibly small, their optical absorption A is evaluated as $A = 1 - R$, where R is the optical reflectance.

3.4 Results and Discussion

3.4.1 SEM Observations

The fabricated local plasmon resonators were observed by SEM. Figure 3.5 shows typical cross-sectional and surface SEM images. The PCL thickness is 120 nm, and the average Au NP thickness is 8.6 nm. The SCL consisting of SiO₂ nanocolumns ~ 50 μm in diameter are prepared on the PCL of the plane SiO₂ layer. On top of the SCL, a two-dimensional array of Au NPs is observed. Consequently, a multilayered Au NP/SCL/PCL/Ag mirror structure was successfully obtained.

3.4.2 Optical Properties

Figure 3.6 shows the typical visual appearance of local plasmon resonators with various Au NP and PCL thicknesses. Using a shutter, the layer thicknesses are successfully modulated on a single substrate at a millimeter scale. The samples are vividly colored according to the PCL thickness because of strong interference. The sample color becomes paler as the Au NP thickness decreases. Figure 3.7 shows the measured optical absorption spectra of the fabricated local plasmon resonators with various average Au NP thicknesses as a function of the photon energy. The PCL thickness is fixed at 120 nm. The yellow region represents high optical absorption. The optical absorption becomes high at a Au NP thickness of around 8 nm, whereas the absorption peak position does not change significantly with the Au NP thickness. These results are consistent with the calculation results in Chapter 2. Figure 3.8 shows the measured optical absorption spectra of the fabricated local plasmon resonators with various PCL thicknesses as a function of the photon energy. The Au NP thickness is fixed at 8.6 nm. Again, the yellow region represents high optical absorption. The obvious stripes as functions of the photon energy and PCL thickness are caused by strong interference. The optical absorption of the fabricated samples varies from ~ 0 to 0.97 depending on the photon energy and PCL thickness. Consequently, samples that have features analogous to those in the calculation results shown in Fig. 2.7 of Chapter 2 are obtained.

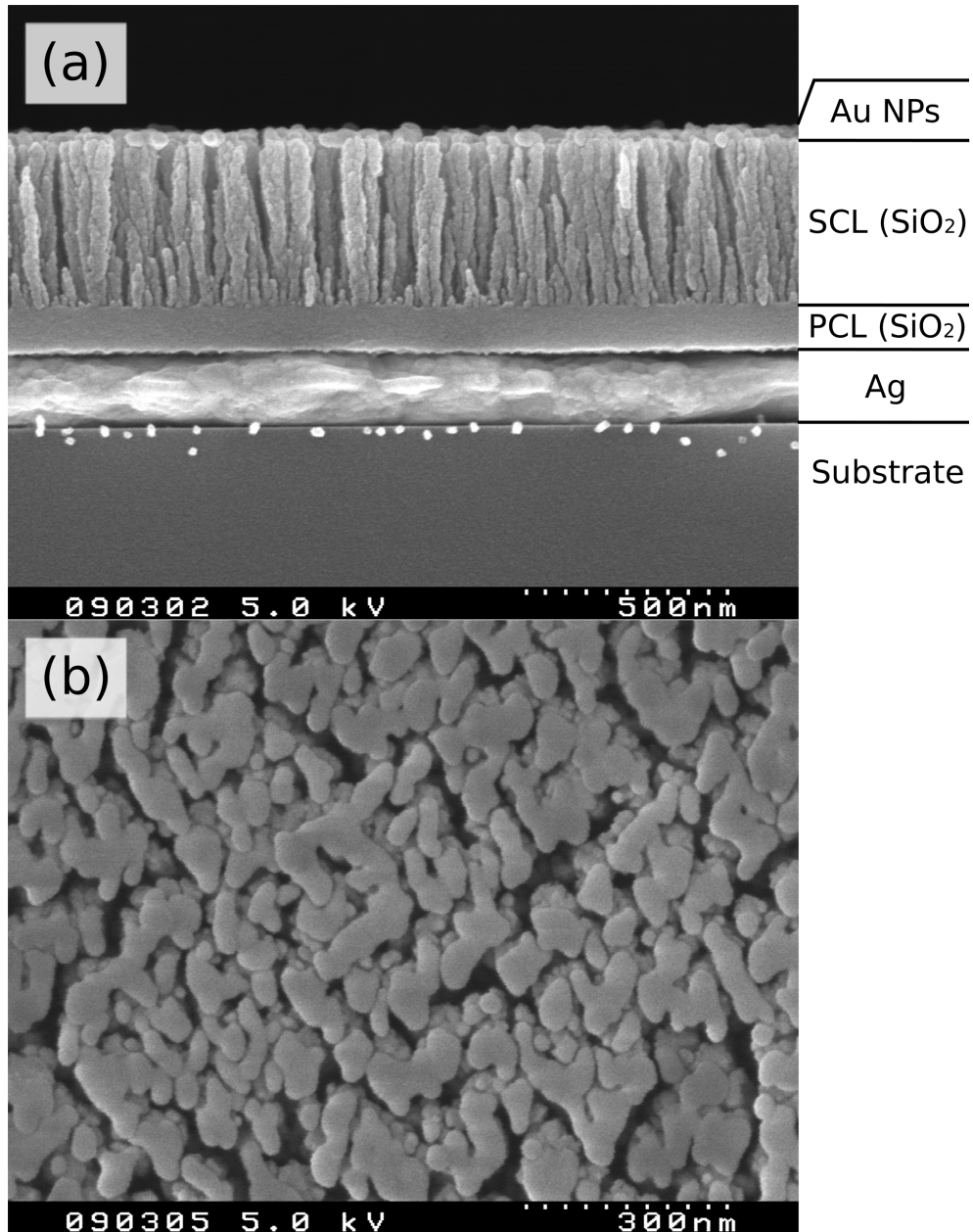


Figure 3.5: Typical SEM images of (a) cross section and (b) surface morphology of the local plasmon resonator.

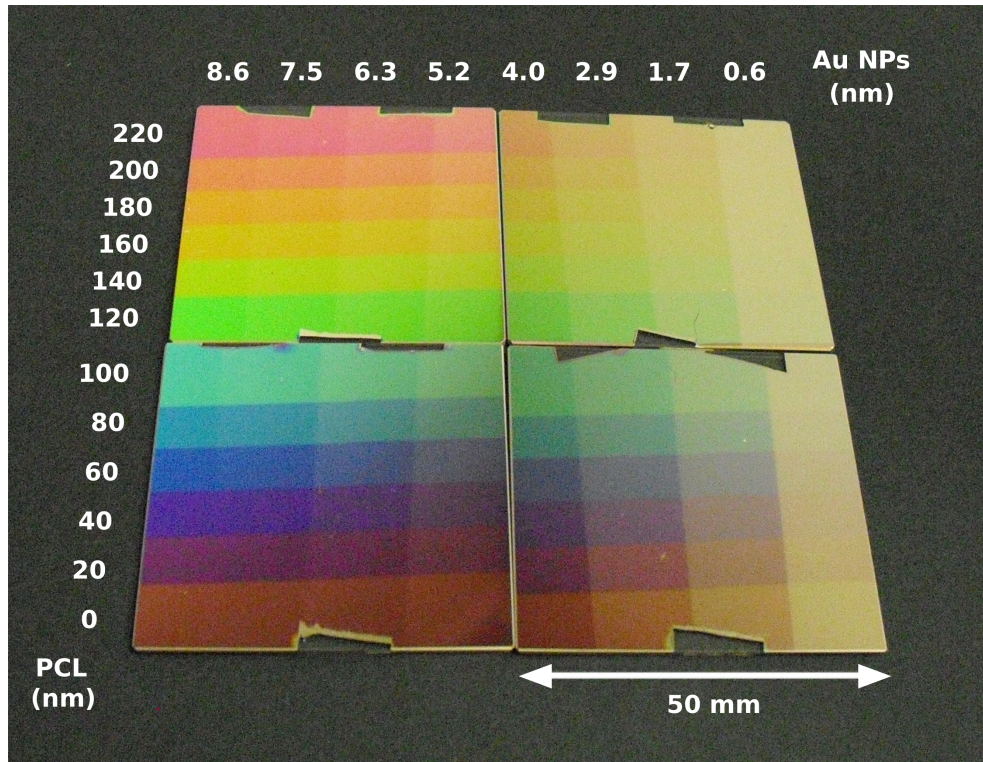


Figure 3.6: Visual appearance of local plasmon resonators with various Au NP and PCL thicknesses.

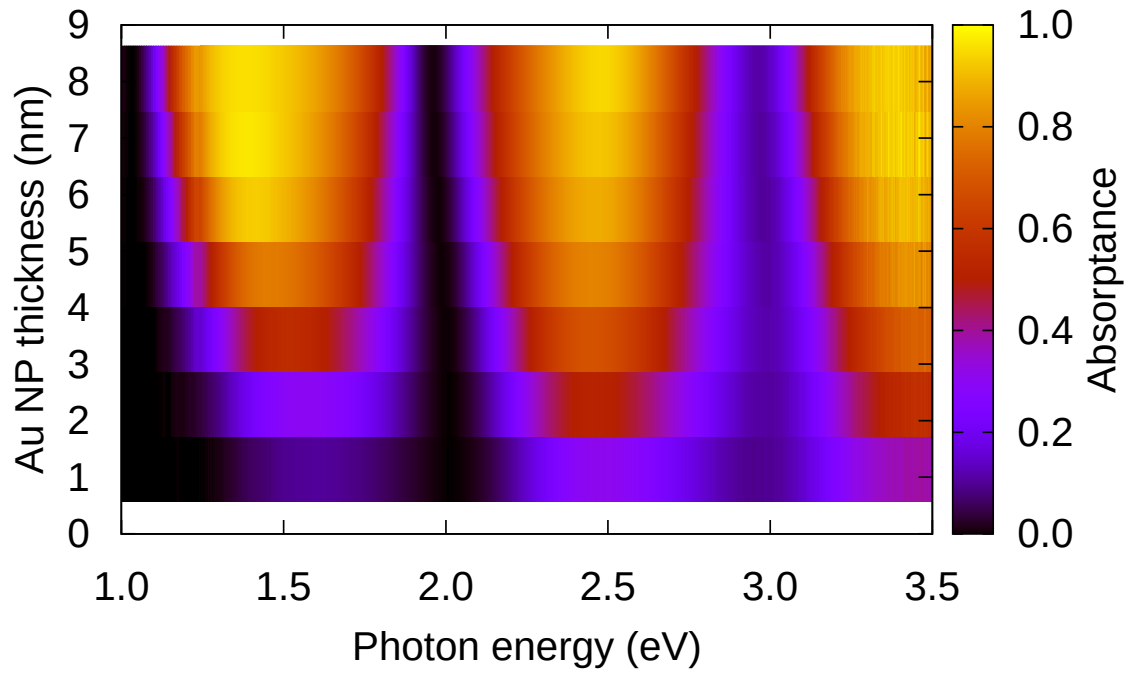


Figure 3.7: Measured optical absorption spectra of local plasmon resonators with various Au NP thicknesses as a function of photon energy. The PCL thickness is fixed at 120 nm.

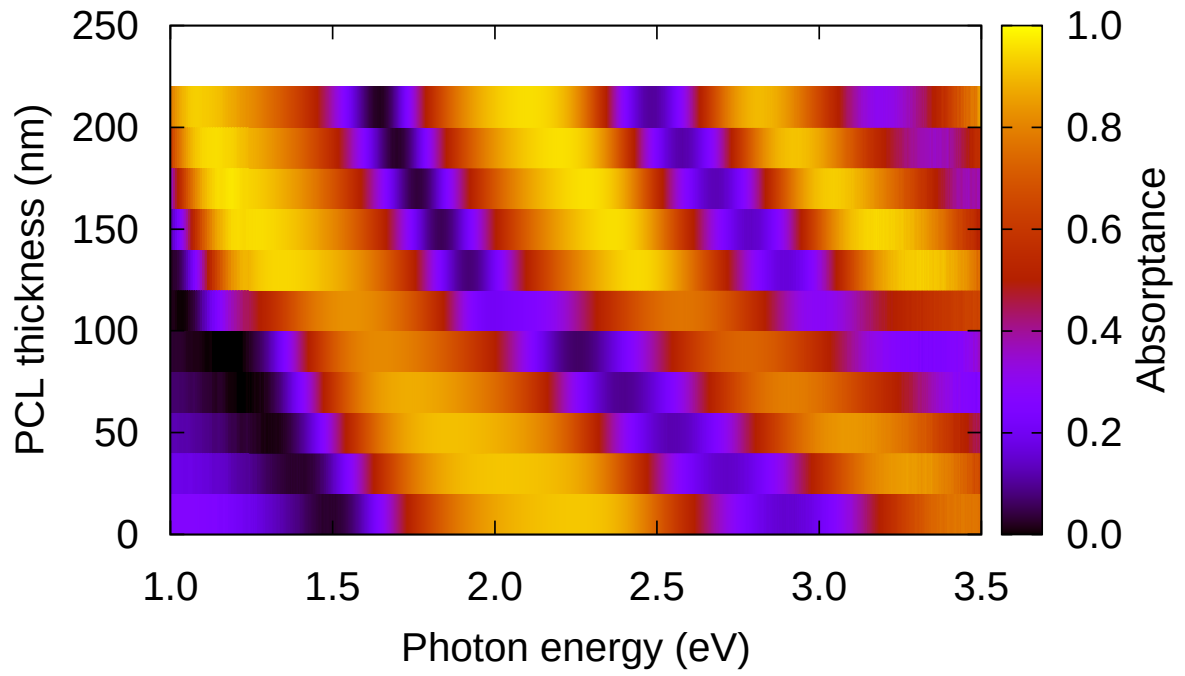


Figure 3.8: Measured optical absorption spectra of local plasmon resonators with various PCL thicknesses as a function of photon energy. The Au NP thickness is fixed at 8.6 nm.

3.5 Conclusion

In this chapter, the detailed fabrication method of local plasmon resonators with Au NP/SiO₂ nanocolumns (SCL)/SiO₂ (PCL)/Ag mirror multilayered structures was described.

The nanocolumns and NP structures were prepared by controlling the deposition angle and in-plane rotation of the substrate during electron beam evaporation of the source materials, which is known as the DOD technique. SEM observations of the fabricated local plasmon resonators showed that layers of SiO₂ nanocolumns and Au NPs with a diameter of ~ 50 nm were successfully obtained.

The optical absorption spectra of local plasmon resonators with various Au NP and PCL thicknesses were evaluated experimentally. When a Au NP thickness of 8.6 nm is chosen, their optical absorption is controlled from ~ 0 to 0.97 by varying the PCL thickness and photon energy owing to interference, which agrees well with the calculation results in Chapter 2.

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Chapter 4

Spatial Controllability of Photothermal Conversion

4.1 Introduction

Photothermal conversion heaters have attracted much attention because of their spatial flexibility in heat generation [1–9]. The heating area can be selected by controlling the position of the laser spot on the photothermal conversion layer, which has been proved to be useful in microfluidic applications [1–9]. However, the difficulty in controlling the shape or pattern of the laser spot limits the improvement of the spatial controllability of temperature gradient.

The local plasmon resonators provide a new approach for the spatial control of the photothermal conversion. In Chapter 3, it has shown that the optical absorption of the local plasmon resonator is controlled between 0 and ~ 0.97 by varying the thickness of the PCL layer. If their photothermal conversion efficiency is controllable by the interference, we can spatially pattern the photothermal conversion area by patterning the PCL thickness (Fig. 4.1(a)). Moreover, by choosing a proper set of PCL thicknesses and incident light wavelength, switching of the photothermal conversion area is expected. For example, only the area A generates heat under a light with a wavelength of λ_a (Fig. 4.1(a)), whereas only the area B generates heat under a light with a wavelength of λ_b (Fig. 4.1(b)).

In this chapter, we investigate the photothermal conversion properties of the local plasmon

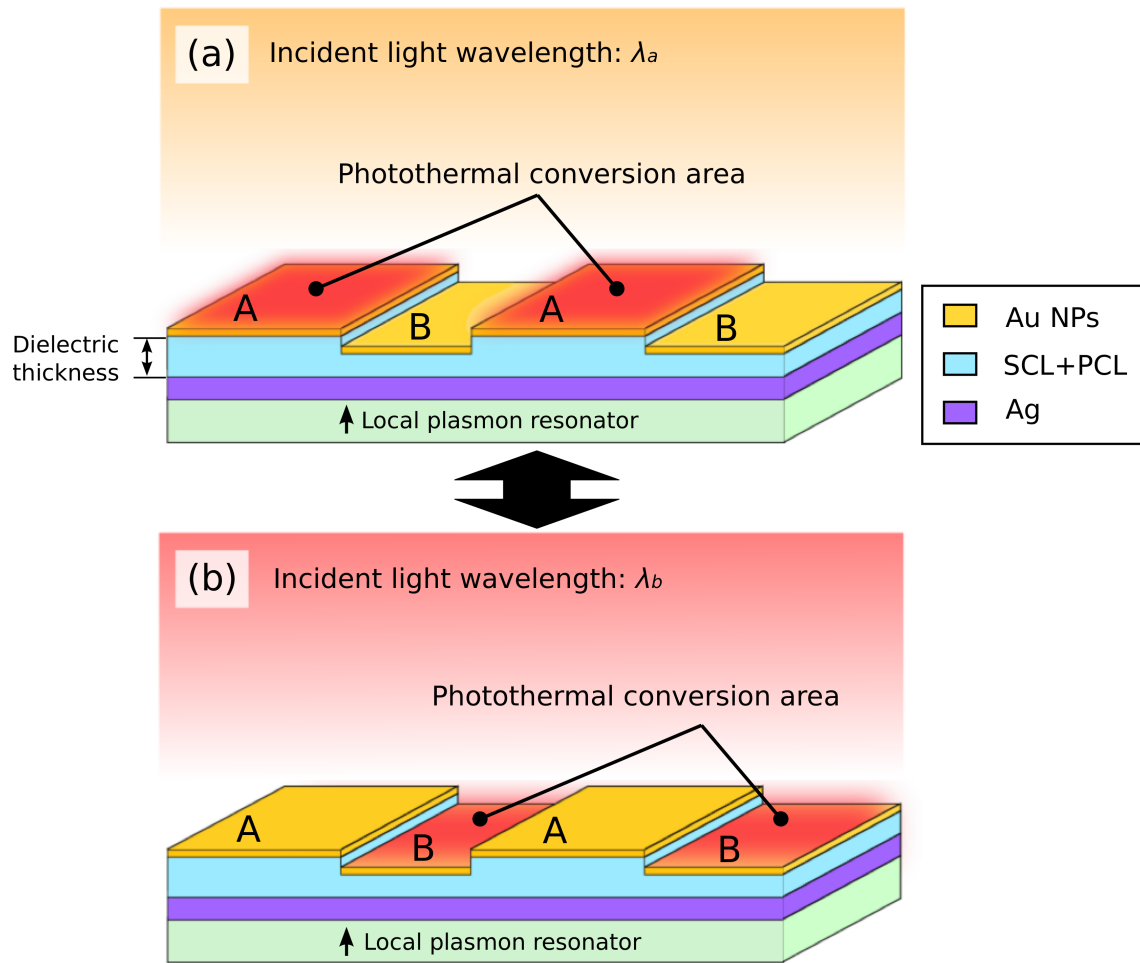


Figure 4.1: Schematic drawing of spatially controlled photothermal conversion by local plasmon resonators.

resonators with various optical absorption under continuous laser irradiation and discuss the spatial controllability of the heat generation.

4.2 Experiments

In order to obtain local plasmon resonator chips with various photothermal conversion efficiencies, we prepared combinatorial local plasmon resonators. We prepared chips with different combinations of Au NP thicknesses and phase control layers on a single substrate of 50×50 mm² by DOD technique. The preparation method of Au NP array is basically the same as that written in Chapter 3. First, a smooth Ag layer of 200 nm thickness was deposited on a glass substrate. On this Ag mirror surface, a PCL of SiO₂ of 0–220 nm thickness was deposited from the normal direction to the surface. A series of different SiO₂ thicknesses were realized on a single substrate by moving a shutter incrementally across the sample during SiO₂ deposition. On the PCL, a SCL of SiO₂ was prepared that was up to 400 nm thick. During the deposition of the PCL, the deposition angle measured from the surface normal was fixed at 80°, and the substrate was rotated continuously and rapidly. A Au NP layer of 0.5–8.6 nm thickness was deposited at a deposition angle of 83.4° onto the shape control layer. A series of different Au NP layer thicknesses were also realized on a single substrate by moving a shutter incrementally. In this way, we prepared local plasmon resonator chips with various combinations of thicknesses of Au and PCL.

Optical reflection measurements on every chip were carried out using a single-beam spectrophotometer in the wavelength range of $300 \text{ nm} < \lambda < 1700 \text{ nm}$. In order to evaluate heat generation from the chips under illumination, we immersed the chips in water and measured the temperature increase of the water. We created a cell (6 mm diameter with a 0.5-mm-thick silicone rubber spacer) on the chip and filled the cell with 14 $\mu\ell$ of water. After the irradiation of the laser ($\lambda = 785 \text{ nm}$) on the local plasmon resonator chip was started, we measured the temperature increase of the water using a thermal viewer (CPA2003, CHINO) until the temperature reached equilibrium. The temperature measurement area is larger than the laser spot which is much smaller than the diameter of the cell.

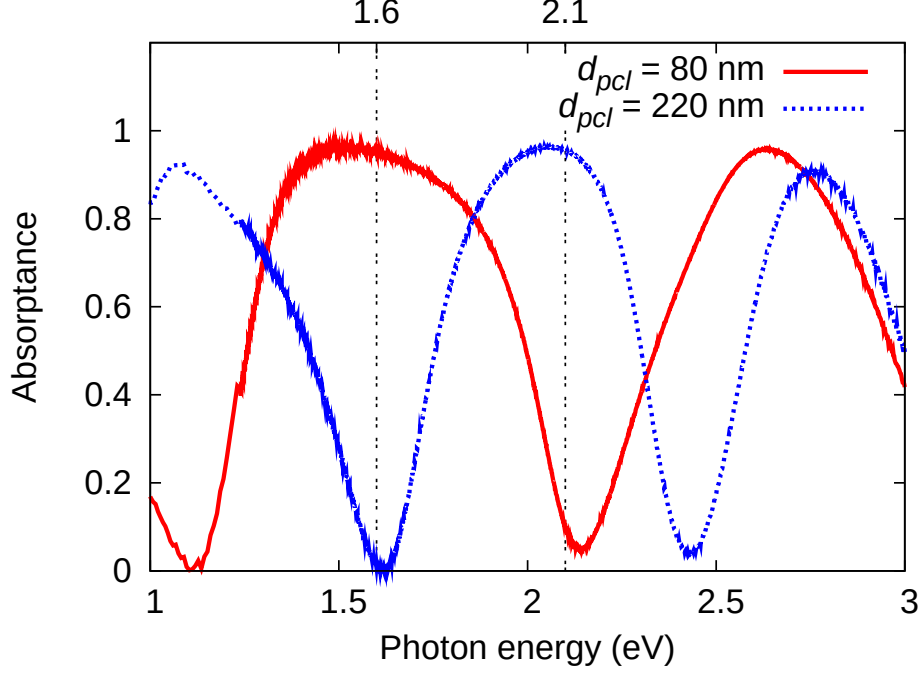


Figure 4.2: Spectrum comparison of local plasmon resonator chips whose PCL thicknesses are $d_{pcl} = 80$ and 220 nm.

4.3 Results and Discussion

4.3.1 Optical Properties

Figure 4.2 depicts the selected absorption spectra of the fabricated local plasmon resonator chips, whose PCL thicknesses, d_{pcl} , are 80 nm and 220 nm. Their Au NP thicknesses are ~ 9 nm. It should be noted that both chips have exactly the same structure except for the thickness of the PCL. Nevertheless, the spectra are very different. The optical absorption of the local plasmon resonator changes between ~ 0 and 0.97 at different photon energies, depending on d_{pcl} . For example, it is remarkable that the optical absorption on $d_{pcl} = 80$ nm becomes greater than 0.95 at a photon energy of around 1.6 eV whereas that on $d_{pcl} = 220$ nm becomes approximately zero at a similar photon energy. On the other hand, at a photon energy of around 2.1 eV, the optical absorption on $d_{pcl} = 220$ nm becomes greater than 0.95 whereas that on $d_{pcl} = 80$ nm becomes less than 0.05 at a similar photon energy. Consequently, the coupling of the light to the local plasmons in Au NPs was successfully modified by interference and spatial control of optical absorption depicted in Fig. 4.1 was shown to be feasible.

4.3.2 Photothermal Response under Continuous Laser Irradiation

Figure 4.3 (a) depicts the typical results of the evaluation of the photothermal conversion, where the temperature increase of the water in the cell created on the local plasmon resonator chip was measured as a function of the irradiation time of the laser. The temperature of the water in the cell begins to increase immediately after the laser irradiation; it reaches equilibrium temperature at an irradiation time longer than 10 s. The equilibrium temperature of the water on the chip with high optical absorption is much higher than that with low absorption. In contrast, the time constant of the temperature increase of the water appears independent of the optical absorption of the chips.

4.3.3 Theoretical Analysis

We discuss the photothermal response of local plasmon resonator chips based on a simple model. We assumed that all of the light energy absorbed by the Au NPs is converted to heat energy and is immediately transferred to the water in the cell. In addition, the energy flowing out of the water in the cell is assumed to be proportional to the difference of the temperature between the water, T , and the surroundings (air and the wall), T_0 . These assumptions allow us to write the rate equation for the temperature of the water in the cell at time t as follows:

$$\frac{dT}{dt} = \frac{1}{CM} (AI - Q(T - T_0)). \quad (4.1)$$

In this equation C , M , A , and I are the specific heat capacity, mass of the water, optical absorption of the chip, and intensity of the laser, respectively. The parameter Q is equivalent to the heat transfer coefficient between the water and the surroundings multiplied by the total surface area of the cell. Thus, the temperature increase of the water in the cell, $T - T_0$, is given by

$$T - T_0 = \frac{AI}{Q} \left(1 - e^{-\frac{Q}{CM}t}\right), \quad (4.2)$$

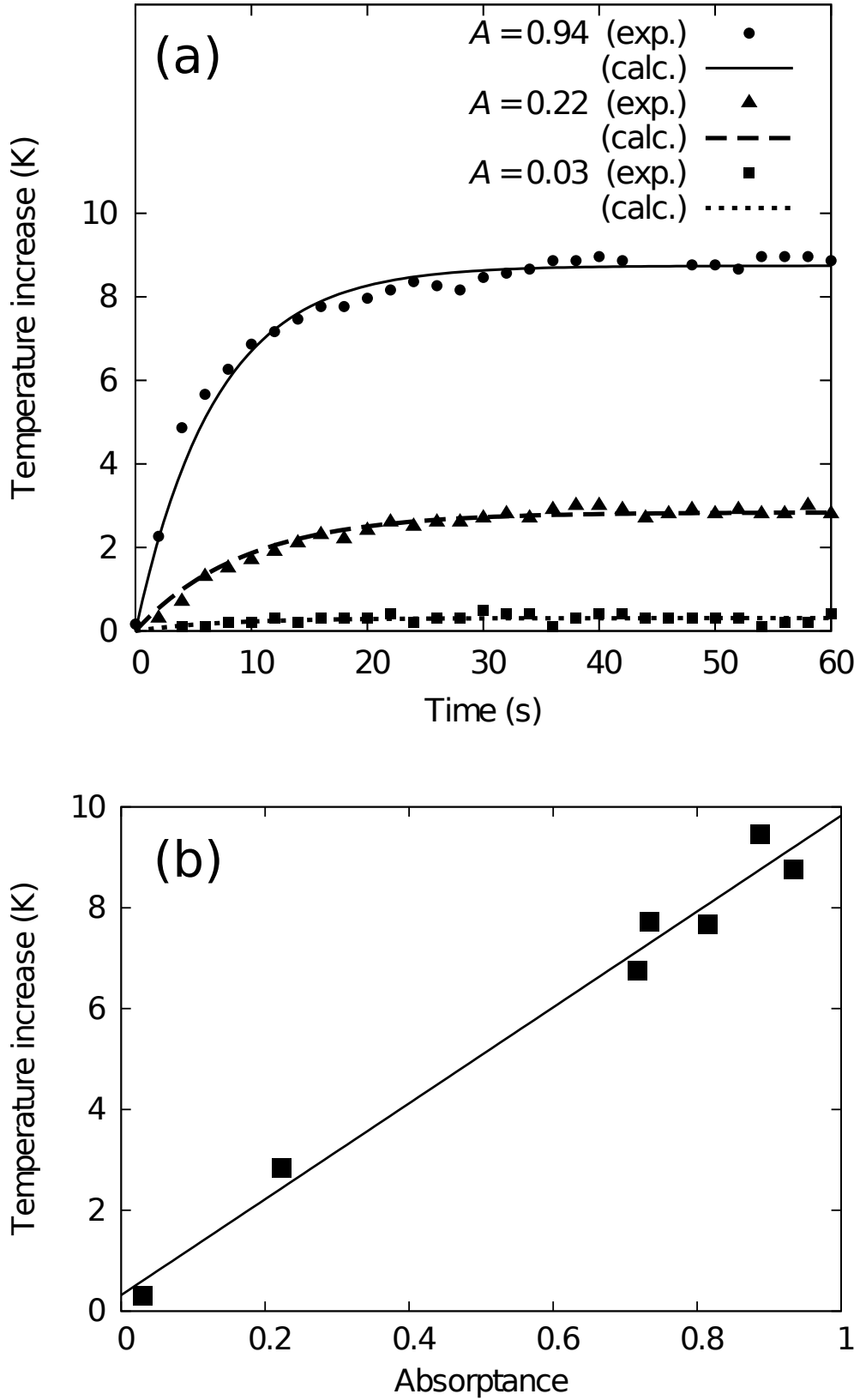


Figure 4.3: Photothermal properties of local plasmon resonators. (a) Trace of the temperature increase of the water in the cell. Both measured and calculated (lines) distributions are shown. (b) The temperature increase of the water in the cell at equilibrium as a function of the optical absorbance. The solid line represents a linear fit, where $Q = 8.4 \text{ mW K}^{-1}$.

where $T = T_0$ at $t = 0$. In the present experiments, $I = 80$ mW and $M = 0.014$ g. According to the literature, the value of C is $4.2 \text{ J g}^{-1} \text{ K}^{-1}$. The optical absorption A is measured on each chip immersed in the water at the wavelength of 785 nm. The lines shown in Fig. 4.3 (a) are the results of fitting Eq. (4.2) with the experimental data, where only Q is a fitting parameter. Remarkably, the calculation agrees well with the measurements. If a significant amount of the heat generated in Au NPs escapes to the ambient medium and is not transferred to the water in the cell, the fitting would become poor. The temperature increase of the water in the cell tends to saturate after ~ 10 s of laser irradiation. Fig. 4.3 (b) shows the equilibrium temperature increase of the water, $(T - T_0)|_{t \rightarrow \infty}$, as a function of the optical absorption A of the chips. Clearly the temperature increase is proportional to the optical absorption and it is consistent with Eq. (4.2). Consequently, the photon energy absorbed into the Au NPs is converted into heat and transferred to the surrounding water efficiently. In addition, we demonstrated that heat generation from the local plasmon resonator can be controlled by tuning the coupling of light to the local plasmons in Au NPs by changing the thickness of the PCL.

In this study, we used cells that are much larger than the common microchannels for the MEMS devices. This large cell size limits the maximum temperature increase of the water in the cell to 10 K and the time constant to 10 s. However, the value of Q may be proportional to the square of the typical length of the cell, so that the equilibrium temperature would be inversely proportional to the square of the length. Thus, the equilibrium temperature could be much higher than 10 K in the small cells or channels. In addition, the time constant may be proportional to the typical length of the cell. Furthermore, the rate of temperature increase is inversely proportional to the cube of the typical length of the cell. Therefore, the temperature change of the water in microchannels will be much faster than that in the cell we used. The local plasmon resonators are expected to be applicable to control the microfluid using photoacoustic generation, thermophoresis, etc.

4.4 Conclusion

In this chapter, the photothermal response of the local plasmon resonators under continuous laser irradiation is investigated. Only by changing the thickness of the PCL can the coupling of light to the local plasmons in Au NPs be successfully controlled. The optical absorption is varied between ~ 0 and 0.97 in the near-infrared region because of strong interference. In addition, heat generation from the local plasmon resonator under illumination (785 nm wavelength) is proportional to the optical absorption. These results suggest that local plasmon resonators can spatially control heat generation flexibly and efficiently. Furthermore, the simple model shows that these resonators modulate the local temperature extremely quickly. The further investigation on the temporal controllability of the local plasmon resonators are provided in Chapter 5.

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Chapter 5

Temporal Controllability of Photothermal Conversion

5.1 Photoacoustic Emission from Local Plasmon Resonators

5.1.1 Introduction

In Chapter 2, the optical absorption of local plasmon resonators having Au NP/PCL/SCL/Ag mirror structures is shown to be highly localized in the thin Au NP layer (~ 10 nm). This result suggests that the photothermal conversion of the local plasmon resonators is expected to be localized at the sample surface and to contribute to rapid modulation of the local temperature. Thus, this chapter investigates the temporal controllability of the heat generation from local plasmon resonators experimentally and theoretically.

To verify the temporal controllability of the local temperature, we focus on the photoacoustic effect [1], whose mechanism is as follows: The light absorbed by a solid is converted into heat and transferred to a surrounding fluid, which subsequently undergoes a volume change. This expanding or contracting fluid layer acts as an acoustic piston and generates acoustic pressure, i.e., photoacoustic emission. The amplitude of this photoacoustic emission is sensitive to the heat flow from the solid to the surrounding fluid. Therefore, the photoacoustic emission at high

Table 5.1: List of samples. (*: PCL thickness.)

	Thickness (nm)	A	Substrate
Local plasmon resonators	0–230*	0.01–0.97	Si wafer
Au	150	0.02	Glass
Ag	150	0.01	Glass
Graphite	Bulk	0.85	–
Si wafer	Bulk	0.67	–

frequency directly indicates the temporal controllability of the surrounding fluid temperature.

The photoacoustic effect is not just a method to analyze photothermal properties of materials. It is expected to be used for many applications in the field of sound-emitting devices [2], photoacoustic imaging [3, 4], and manipulation of fluid or particles [5–7]. Therefore, if strong photoacoustic emission compared to bulk absorbing layer is demonstrated, the local plasmon resonators will find wide application as an acoustic emitter.

In this section, the photoacoustic emission from local plasmon resonators with various optical absorption properties and that from bulk absorbing materials are compared to show the temporal controllability of photothermal conversion in local plasmon resonators.

5.1.2 Experiments

The samples prepared for the photoacoustic measurements are listed in Table 5.1. The local plasmon resonators were self-assembled by the DOD technique (see Chapter 3). First, a 200-nm-thick smooth Ag layer and a PCL of SiO₂ with thicknesses of 0–230 nm were deposited on a Si wafer. On the PCL, a 300-nm-thick SCL of SiO₂ was prepared. During SCL deposition, the deposition angle measured from the surface normal was fixed at 80°, and the substrate was continuously and rapidly rotated. A Au NP layer was deposited at a deposition angle of 83.4° on the SCL. The average thickness of the deposited Au was ~ 7 nm. Optical reflection measurements of the fabricated samples at an incidence angle of 2° were made using a single-beam spectrophotometer with a wavelength range of $300 \text{ nm} < \lambda < 1700 \text{ nm}$. Local plasmon resonators with a wide range of optical absorption (0.01–0.97) were obtained.

The Au and Ag thin films were prepared by simple deposition on a glass substrate up to 150 nm thick. In addition, small pieces of graphite and Si wafer were also prepared as specimens

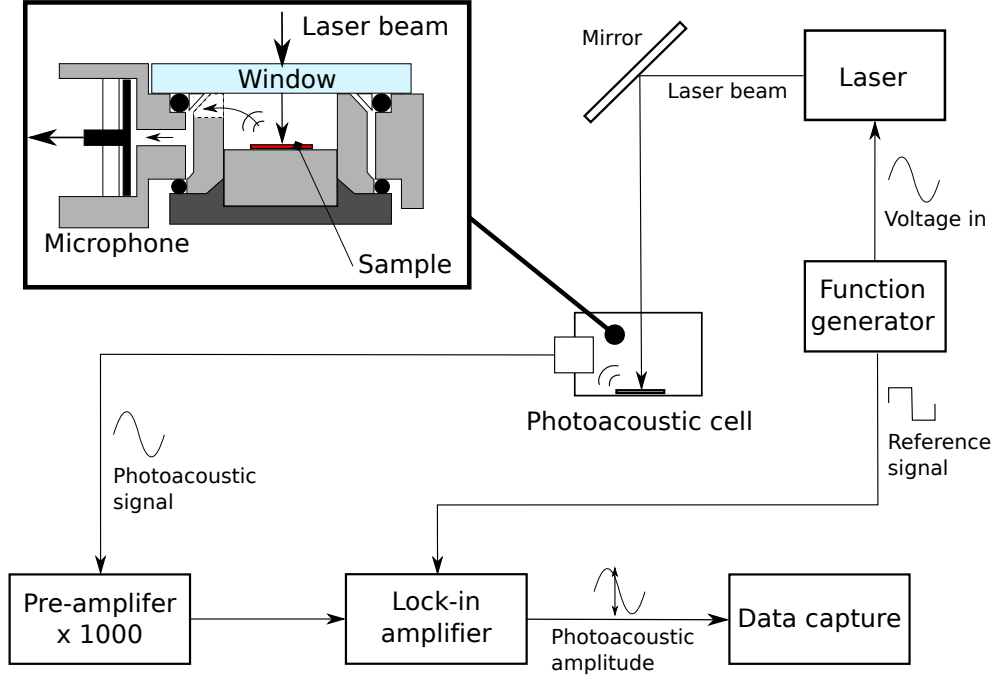


Figure 5.1: Experimental setup for photoacoustic measurements.

of bulk absorbing material.

Photoacoustic measurements of the samples, which were cut into chips with dimensions of $4 \text{ mm} \times 4 \text{ mm} \times 0.5 \text{ mm}$, were performed using a photoacoustic cell (MTEC Model 300, Fig. 5.1). We loaded a sample into the photoacoustic cell, which is 10.0 mm in diameter and 3.5 mm in height and is filled with air. The chip was then irradiated with a laser (wavelength 785 nm), whose intensity was modulated sinusoidally, from the surface normal direction. The photoacoustic signal, which was detected by a microphone equipped in the photoacoustic cell, was measured with a lock-in amplifier (LI 5640, NF) and recorded as a function of the laser modulation frequency over a range of 1–100 kHz.

5.1.3 Results and Discussion

Figure 5.2(a) shows photoacoustic spectra of a local plasmon resonator ($A = 0.79$) and a Si wafer ($A = 0.67$) measured using an air-filled photoacoustic cell. Those spectra have several distinct peaks at identical positions. The positions of those peaks were changed significantly by changing the purge gas in the photoacoustic cell from air to helium [Fig. 5.2(b)], which suggests that the peaks in the photoacoustic spectra originate from acoustic resonance in the photoacoustic cell. For example, the peak at 3.6 kHz in Fig. 5.2(a) is shifted to 9.6 kHz

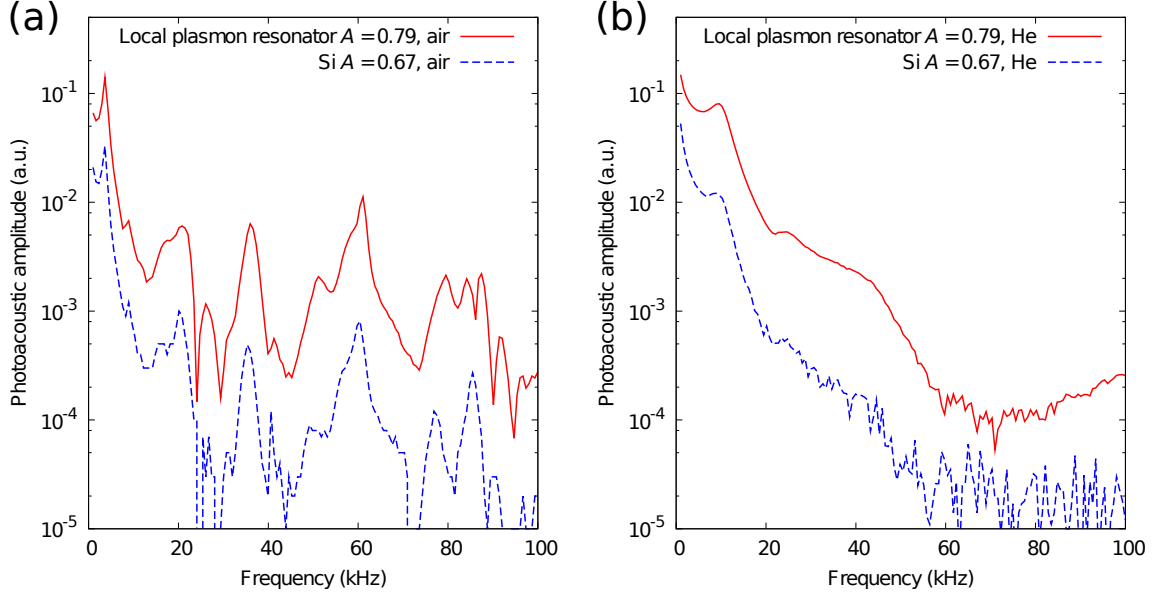


Figure 5.2: Photoacoustic spectra of a local plasmon resonator ($A = 0.79$) and a Si wafer ($A = 0.67$) measured in (a) an air atmosphere and (b) a helium atmosphere.

in Fig. 5.2(b). These peak positions are almost proportional to the acoustic velocity in the corresponding purge gas (343 m s^{-1} in air and 1001 m s^{-1} in helium, at room temperature and 1 atm [8]). Because the acoustic resonance peak positions are sensitive to the shape of the photoacoustic cell, and the resonance mode is complex, especially at high frequency, the absolute peak intensities are not attractive for evaluation of the photoacoustic properties of the samples. Apart from the resonance peaks inherent in the photoacoustic system used here, we focused on the relative amplitudes of the obtained spectra, which qualitatively describe the surface temperature modulation of the samples.

Figures 5.3(a) and 5.3(b) show photoacoustic spectra from the samples listed in Table 5.1 measured using an air-filled photoacoustic cell. The local plasmon resonator with the higher optical absorption generates more photoacoustic emission, and the local plasmon resonator with high optical absorption ($A = 0.97$) generates almost two orders of magnitude more photoacoustic emission than that with low optical absorption ($A = 0.01$). To compare these photoacoustic spectra quantitatively, the photoacoustic amplitude of each sample at 60 kHz is plotted in Fig. 5.4. The photoacoustic amplitude of the local plasmon resonators (red circles) is proportional to their optical absorption, which suggests that the measured acoustic signal corresponds to the photoacoustic emission due to photothermal conversion in the samples.

Figure 5.3(b) shows the photoacoustic spectra of the local plasmon resonators ($A = 0.97$ and 0.50), graphite sample, Si wafer, Au thin film, and Ag thin film. The local plasmon resonator with high optical absorption ($A = 0.97$) generates almost two orders of magnitude more photoacoustic emission than the highly reflective Ag thin film ($A = 0.01$) and Au thin film ($A = 0.02$). Additionally, the sample with $A = 0.97$ generates a photoacoustic amplitude 15 times larger than that of the Si wafer ($A = 0.67$) and 8 times larger than that of the graphite ($A = 0.85$). The remarkable feature is that the photoacoustic amplitude of the sample with $A = 0.50$ is 8 times larger than that of the Si wafer which has higher optical absorption than the sample. Figure 5.4 clearly shows this difference, and the photoacoustic amplitude of the Si wafer is even smaller than that of the local plasmon resonator with $A = 0.14$. These results indicate that the localized heat generation in the Au NP layer, which is much thinner than the photothermal conversion layer of the Si wafer ($\sim 9 \mu\text{m}$ thick), contributes to the efficient photoacoustic emission (see Chapter 2). Consequently, highly localized heat generation in the Au NPs enables rapid temperature gradient modulation near the local plasmon resonator surface.

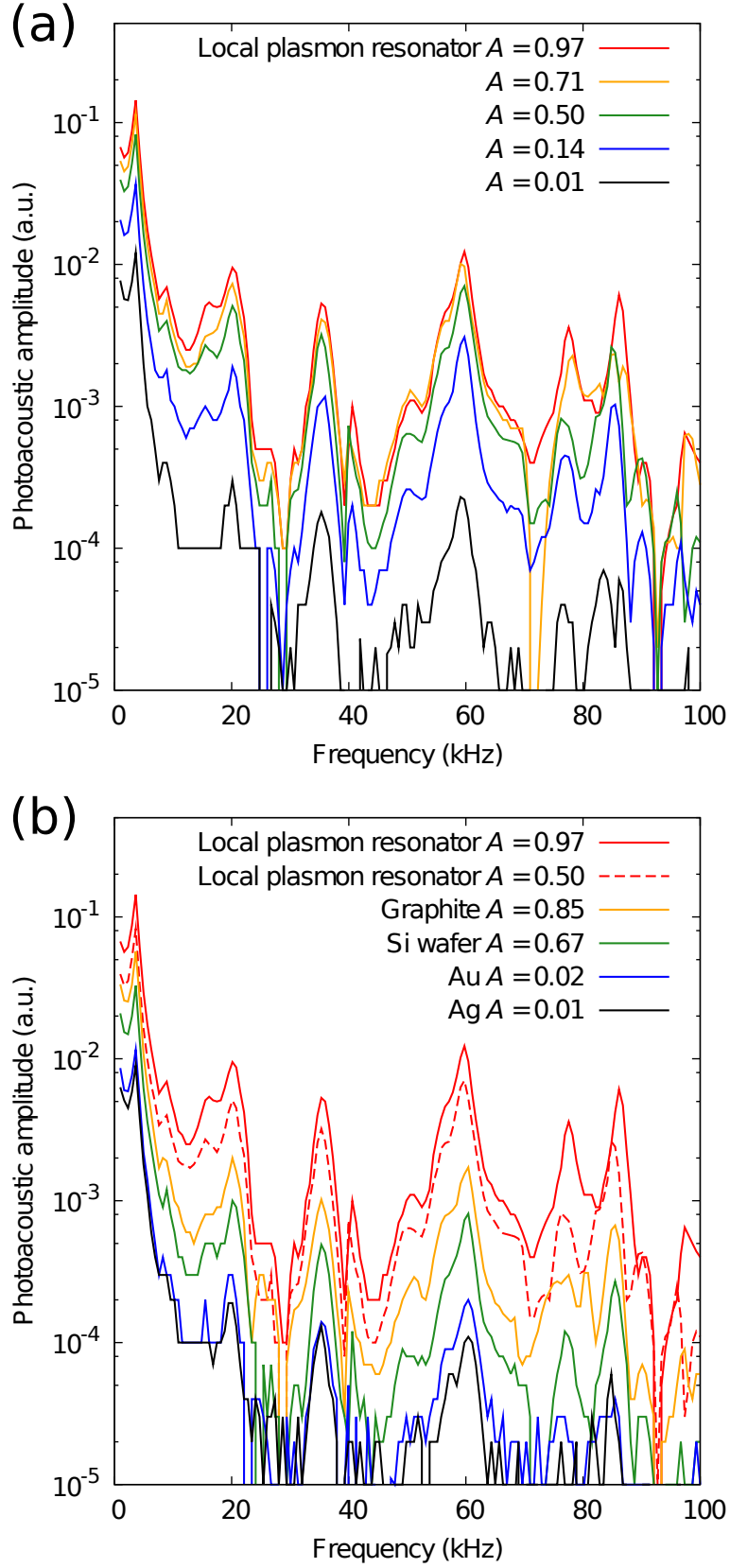


Figure 5.3: Photoacoustic spectra of (a) local plasmon resonators with various optical absorption values ($A = 0.01$ – 0.97) at a wavelength of 785 nm and (b) local plasmon resonators with $A = 0.50$ and $A = 0.97$, graphite ($A = 0.85$), Si wafer ($A = 0.67$), Au thin film ($A = 0.02$), and Ag thin film ($A = 0.01$).

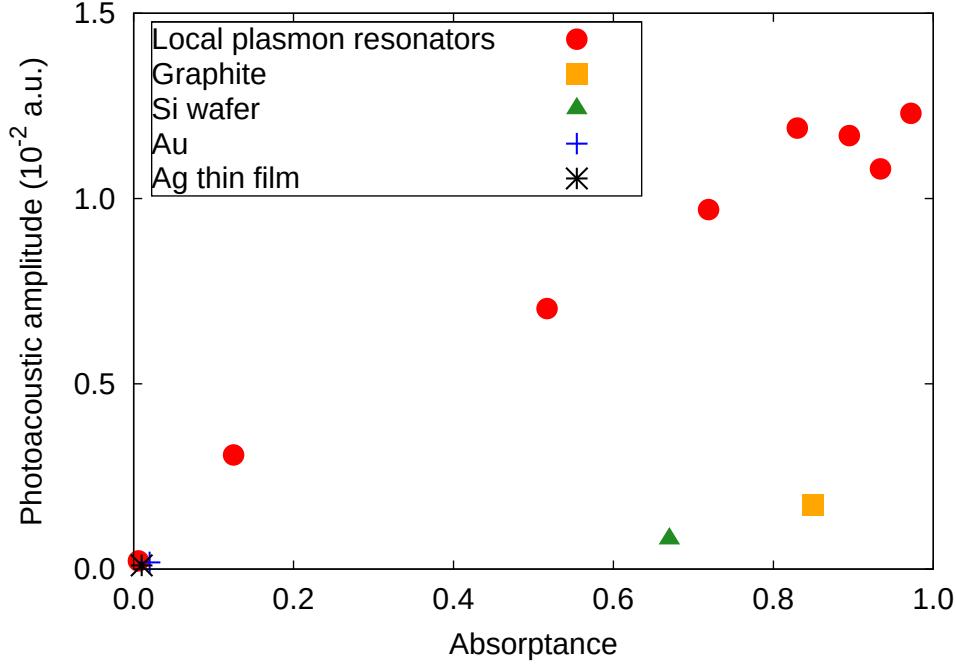


Figure 5.4: Photoacoustic amplitude of local plasmon resonators with various optical absorption, graphite ($A = 0.85$), Si wafer ($A = 0.67$), Au thin film ($A = 0.02$), and Ag thin film ($A = 0.01$) at the laser modulation frequency of 60 kHz as a function of their optical absorption at the wavelength of 785 nm.

5.1.4 Conclusion

In this section, the photoacoustic emission from local plasmon resonators was investigated experimentally. The photoacoustic amplitude of the local plasmon resonators with low optical absorption ($A = 0.01$) is of the same order as that of highly reflective 150-nm-thick Ag and Au thin films. On the other hand, the photoacoustic amplitude of the local plasmon resonator with high optical absorption ($A = 0.97$) is 15 times larger than that of the bulk Si wafer ($A = 0.67$) and 8 times larger than that of graphite ($A = 0.85$). These results suggest that the photothermal conversion of the local plasmon resonator is localized in the thin Au NP layer (~ 10 nm), which enables rapid modulation of the temperature of the surrounding fluid compared to bulk absorbing materials. Local plasmon resonators are desirable as nano-heaters which can control local temperatures with a high degree of sensitivity.

Table 5.2: The list of samples, where α represents the deposition angle.

	With SCL		Without SCL	
	Thickness (nm)	α (°)	Thickness (nm)	α (°)
Au NP layer	9.8	83.4	9.8	83.4
SCL (SiO ₂)	340	78.6	–	–
PCL (SiO ₂)	0–280	0	310–500	0
Ag mirror	200	0	200	0

5.2 Effect of Thermal Conductivity on Photoacoustic Emission

5.2.1 Introduction

In Section 5.1, the local plasmon resonator was shown to generate 8 times larger photoacoustic emission than the bulk absorbing graphite. We attributed this efficient photoacoustic emission to the highly localized photothermal conversion in Au NP layer, which contributes to the rapid heat transfer from the sample to the surrounding fluid. Another important factor to the photoacoustic amplitude is thermal properties of the sample. It is known that the efficiency of the thermally induced acoustic emission from a thin metal film is largely dependent on the thermal properties of the underlying layer [9]. Therefore, for local plasmon resonators, we expect highly amplified photoacoustic emission from the Au NP arrays owing to the thermal insulating effect of the porous SiO₂ layer.

In this section, we compare the photoacoustic emission from local plasmon resonators with and without porous SCL layer experimentally. In addition, their photoacoustic emission is discussed based on a one-dimensional heat transfer model in order to verify the contribution of the thermal conductivity of the samples.

5.2.2 Experiments

We prepared local plasmon resonators with Au NPs/SCL/PCL/Ag mirror structure (Fig. 5.5) by using DOD (see Chapter 3). The local plasmon resonators were prepared by electron beam evaporation under a pressure of 5×10^{-4} Pa with a deposition rate of 0.2–0.3 nm s^{−1}. First,

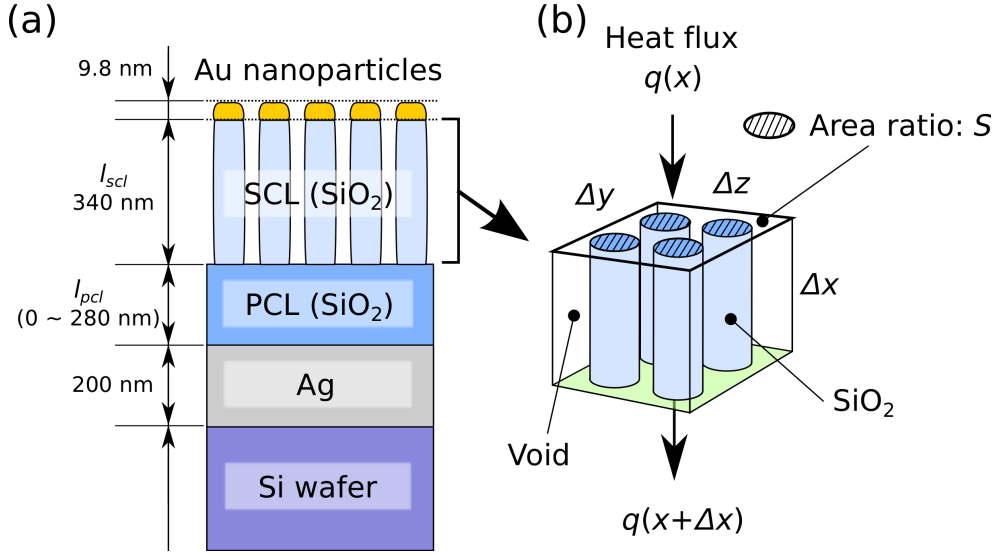


Figure 5.5: (a) Schematic drawing of side view of local plasmon resonator with Au NP array/SCL/PCL/Ag mirror structure. (b) Volume element of the SCL with cylindrical columns. The filling factor, S , is equal to the area ratio.

a smooth Ag layer with 200 nm thickness was deposited on a Si wafer. Onto this Ag mirror surface, a PCL of SiO₂ was deposited with the vapor normally incident to the surface. The PCL thickness, l_{pcl} , was varied from 0 nm to 280 nm as listed in Table 5.4 in order to obtain samples with a wide range of optical absorption. This series of different SiO₂ thicknesses were realized on a single substrate by moving a shutter incrementally across the sample during SiO₂ deposition. On the PCL, a SCL of SiO₂ was prepared; this layer was evaporated until it reached a thickness of 340 nm. During the deposition of the SCL, the deposition angle (measured as an angle from the normal) was fixed at 78.6° and the substrate was rotated continuously and rapidly. A Au NP layer with 9.8 nm thickness was deposited at a deposition angle of 83.4° onto the SCL. In order to investigate the contribution of the porous SCL layer to the photoacoustic amplitude, we also prepared local plasmon resonators without an SCL. In the case of the preparation of samples without an SCL, the step of SCL deposition was skipped and the PCL thickness was varied from 310 nm to 500 nm. The optical reflection measurements at an angle of incidence of 2° were carried out using a single-beam spectrophotometer in the wavelength range of 300 nm < λ < 1700 nm. Since the optical transmittance and scattering of our samples are negligibly small, their optical absorption A is evaluated as $A = 1 - R$, where R is the optical reflectance.

The photoacoustic measurements were performed using a photoacoustic cell (10.0 mm in

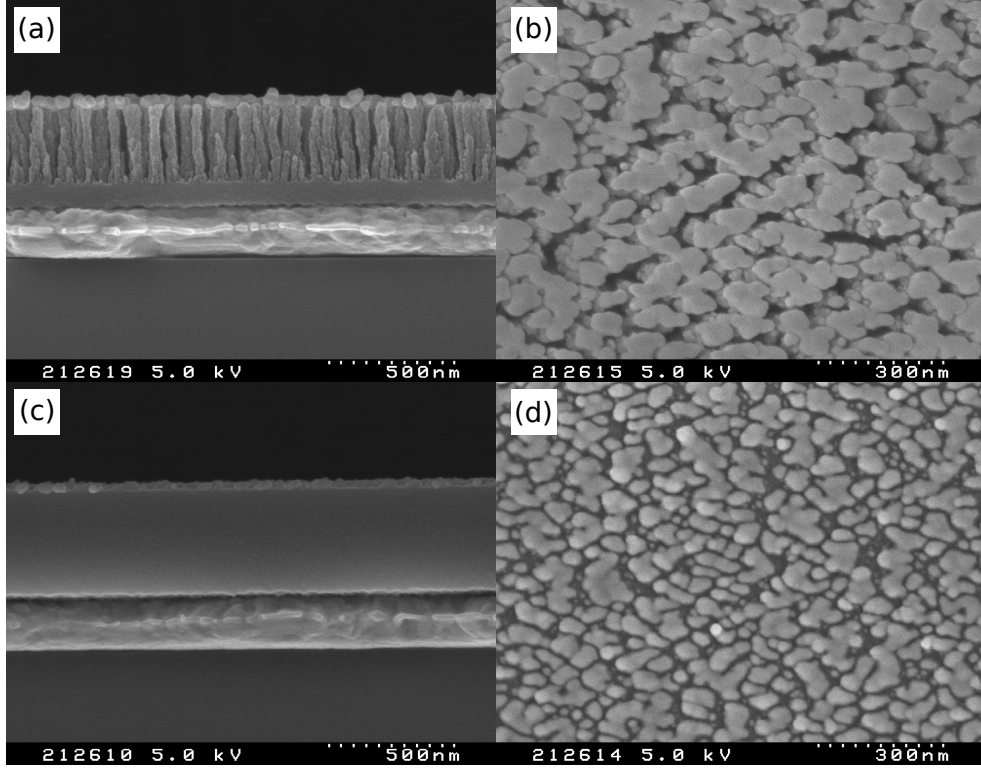


Figure 5.6: SEM images of (a) the cross section and (b) the surface morphology of the local plasmon resonator with a Au NP/SCL/PCL/Ag mirror structure. (c) and (d) SEM images of the sample with a Au NP/PCL/Ag mirror structure.

diameter and 3.5 mm height, Fig. 5.1) on the local plasmon resonators with and without SCL, bulk graphite, and Ag thin film. The experimental setup used for the measurements is depicted in Fig. 5.1. We loaded the sample, which was cut into a small piece of $4\text{ mm} \times 4\text{ mm} \times 0.5\text{ mm}$ size, onto the photoacoustic cell filled with air. Then, the chip was irradiated with a laser (wavelength 785 nm), whose intensity was modulated sinusoidally, from the surface normal. The photoacoustic signal detected by a microphone was measured with a lock-in amplifier and recorded as a function of the laser modulation frequency over the range from 1 kHz to 100 kHz.

5.2.3 Results and Discussion

5.2.3.1 Effect of Porous SiO_2 Layer

Figure 5.6 show typical SEM images of the prepared local plasmon resonators with and without SCL. From the SEM image of the cross section of each sample (Figs. 5.6(a) and 5.6(c)), it is clear that the multilayered structures of Au NP layer/ SiO_2 dielectric layer/Ag mirror are realized by DOD. In the case of the Au NP layers, the local plasmon resonator with an SCL has a porous

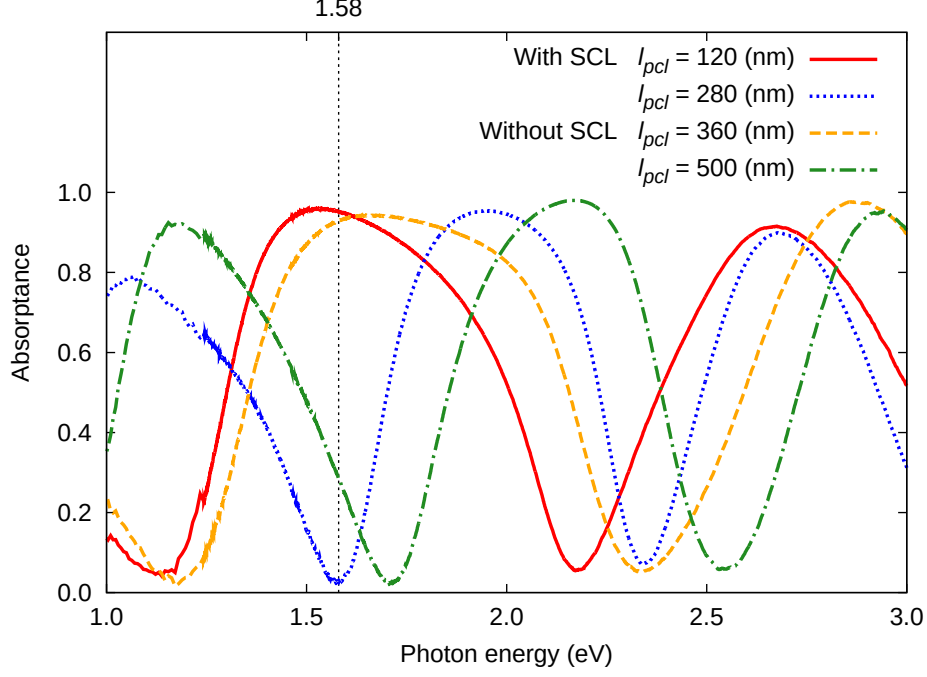


Figure 5.7: Optical absorption spectra of the local plasmon resonators with an SCL ($l_{pcl} = 120$ nm and 280 nm thickness) and without an SCL ($l_{pcl} = 360$ nm and 500 nm thickness)

SiO₂ layer (340 nm thick), whereas the sample without the SCL has no pores in the dielectric layer. However, the thicknesses of the Au NP layers are equally small regardless of the existence of the SCL. In addition, as shown in Figs. 5.6(b) and 5.6(d), granular morphology is realized in the samples with and without SCL. Although the structures in Fig. 5.6(b) are slightly larger than those in Fig. 5.6(d), heat transfer from Au NPs to air may not drastically differ depending on the existence of the SCL.

Figure 5.7 shows the optical absorption spectra of the local plasmon resonators with and without an SCL. The optical absorption of the local plasmon resonators changes periodically as a function of the photon energy, and the absorption peaks change drastically with the PCL thickness. These spectral properties originate from the interference [10–12] and can be understood by multilayered homogeneous layers at least around NIR or longer wavelength region because dimensions of the nanostructures in the layers are much smaller than that of the wavelength. In those wavelength region, the Au NP layer is treated as an effective medium which includes the material with a constant permittivity and Au NPs of which dielectric function is represented by the Drude model. The SCL is also treated as a homogeneous medium of which permittivity is 1.20–1.25. The PCL and the Ag mirror are of course uniform SiO₂ and

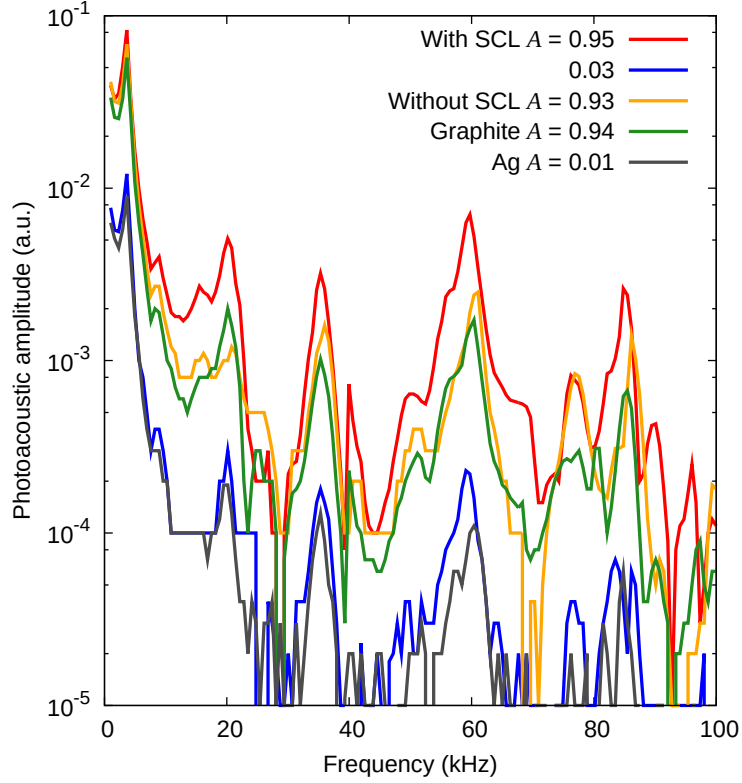


Figure 5.8: Photoacoustic spectra of the local plasmon resonators with an SCL ($A = 0.95$ and 0.03) and without an SCL ($A = 0.93$), in addition to those of graphite ($A = 0.94$) and Ag ($A = 0.01$).

Ag layers. The details have been reported in the previous paper [10] for Ag NPs/dielectric spacer/Ag mirror structures, which is essentially identical with the structures in the present study. In the Fig. 5.7, the coupling of the light to the local plasmons in Au NPs is successfully modified, regardless of the existence of the SCL. At the wavelength of 785 nm (1.58 eV) in the photoacoustic measurements, the optical absorption, A , of the prepared local plasmon resonators with the SCL changes from 0.03 to 0.95, while that of the samples without the SCL changes from 0.28 to 0.93.

We performed photoacoustic measurements on the local plasmon resonators in order to evaluate the contribution of their optical absorption and of the porous SCL to the photoacoustic amplitude. Figure 5.8 shows the typical photoacoustic spectra of the local plasmon resonators with an SCL ($A = 0.95$ and 0.03) and without an SCL ($A = 0.93$), in addition to the photoacoustic spectra of graphite ($A = 0.95$) and Ag ($A = 0.01$). In the spectra, many distinct peaks are observed. Since the peak positions are independent of the samples, the peaks originate from the acoustic resonance in the photoacoustic cell. However, as indicated in Fig. 5.1, the shape

of the photoacoustic cell is too complex to analyze its resonance modes. Thus, we focus our attention on the relative amplitudes of the obtained spectra.

In Fig. 5.8, the photoacoustic amplitude, P , of the local plasmon resonator with an SCL having high optical absorption ($A = 0.95$) is approximately eight times larger than that of graphite ($A = 0.94$) and three times larger than that of the sample without an SCL ($A = 0.93$). On the other hand, the signal from the sample with an SCL having low absorption ($A = 0.03$) has the same order of magnitude as that from the high reflective Ag thin film ($A = 0.01$). These results suggest that the local plasmon resonators with an SCL can realize efficient photoacoustic emission and spatial modulation by the tuning of the thickness of the PCL.

In order to understand the effect of nanostructures on the photoacoustic properties, we focused our attention on the properties of two series of samples with and without an SCL. For both series of samples, we successfully realized the similar ranges of $310 < l_{pcl} + l_{scl} < 510$ nm and $0.25 < A < 0.95$, while the amount of deposited Au was kept constant at 9.8 nm. Figure 5.9 show some of the photoacoustic spectra of those local plasmon resonators, with an SCL (Fig. 5.9(a)) and without an SCL (Fig. 5.9(b)), as a function of the laser modulation frequency. The signal amplitude of the samples with the SCL varies significantly depending on the sample, while that of the samples without the SCL varies only slightly. For quantitative comparison, we listed photoacoustic amplitude at the laser modulation frequency of 60 kHz, optical absorption, l_{scl} , and l_{pcl} of all samples in Table 5.3. The value of P seems to show a monotonic increase with an increasing A . However, it is worth noting that the photoacoustic amplitude of the Au NP array depends not only on A but also on the thickness of the underlying dielectric layer [1]. Since the heat generated from the Au NPs is expected to be proportional to their optical absorption [12], we plotted the ratio of P at the laser modulation frequency of 60 kHz to A , for each sample, as a function of the dielectric thickness, $l_{pcl} + l_{scl}$ (Fig. 5.10). The value of P/A is almost independent of the thickness of the dielectric layer. This supports the result that P is essentially proportional to A . On the other hand, P/A is highly sensitive to the existence of the porous SCL, and the local plasmon resonators with an SCL are capable of producing photoacoustic signals with an approximately threefold higher amplitude than those without an SCL.

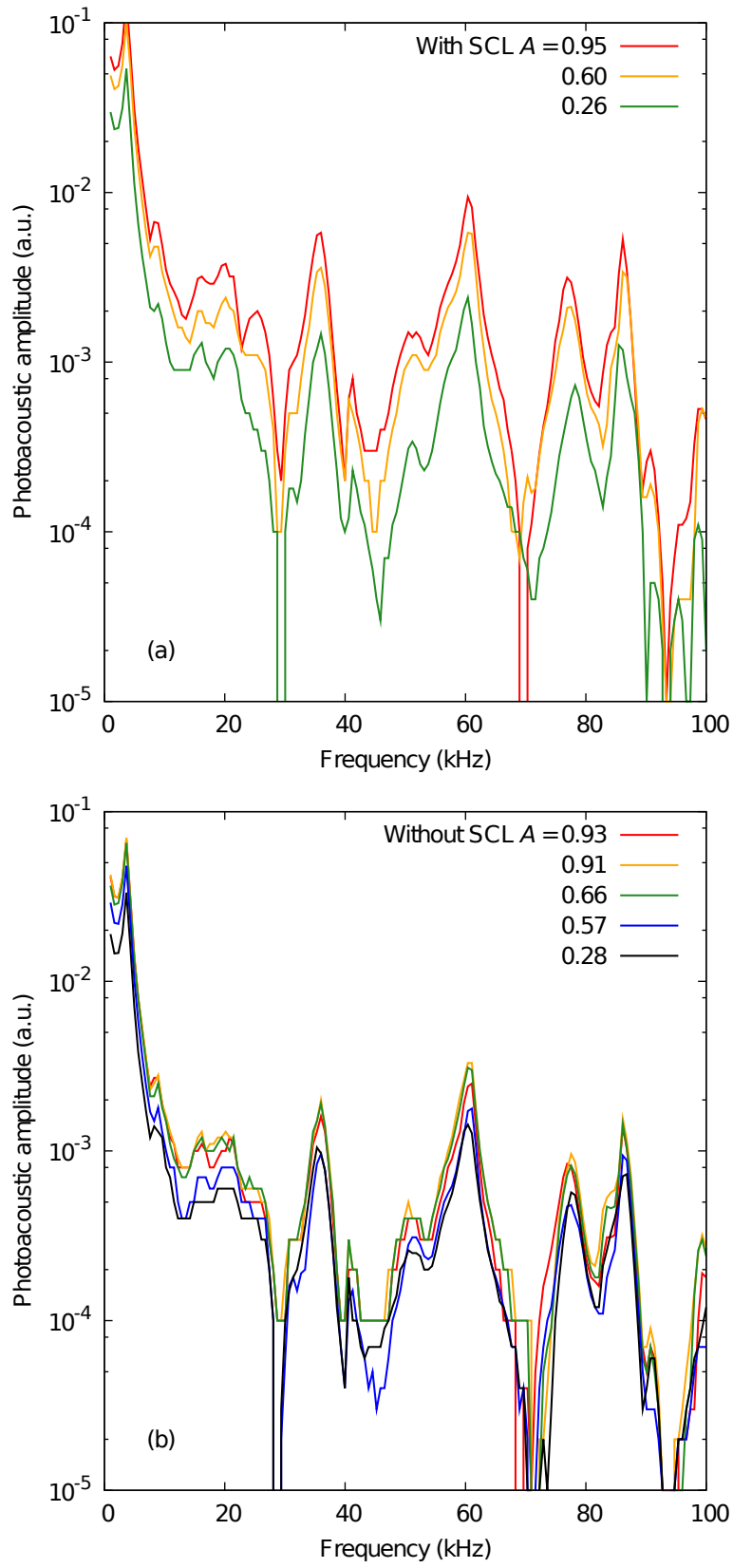


Figure 5.9: Typical photoacoustic spectra of local plasmon resonators, (a) with an SCL and (b) without an SCL, for various optical absorption values.

Table 5.3: Properties of the local plasmon resonators with and without an SCL.

	P at 60 kHz (10^{-2} a.u.)	A	l_{scl} (nm)	l_{pcl} (nm)
With SCL	1.07	0.95	340	132
	0.92	0.92	340	110
	1.18	0.94	340	88
	1.07	0.95	340	88
	0.94	0.95	340	82
	0.96	0.93	340	71
	1.20	0.88	340	66
	0.97	0.94	340	66
	0.83	0.82	340	44
	0.58	0.60	340	22
	0.24	0.26	340	0
Without SCL	0.24	0.93	0	360
	0.33	0.91	0	410
	0.31	0.66	0	460
	0.17	0.57	0	505
	0.14	0.28	0	310

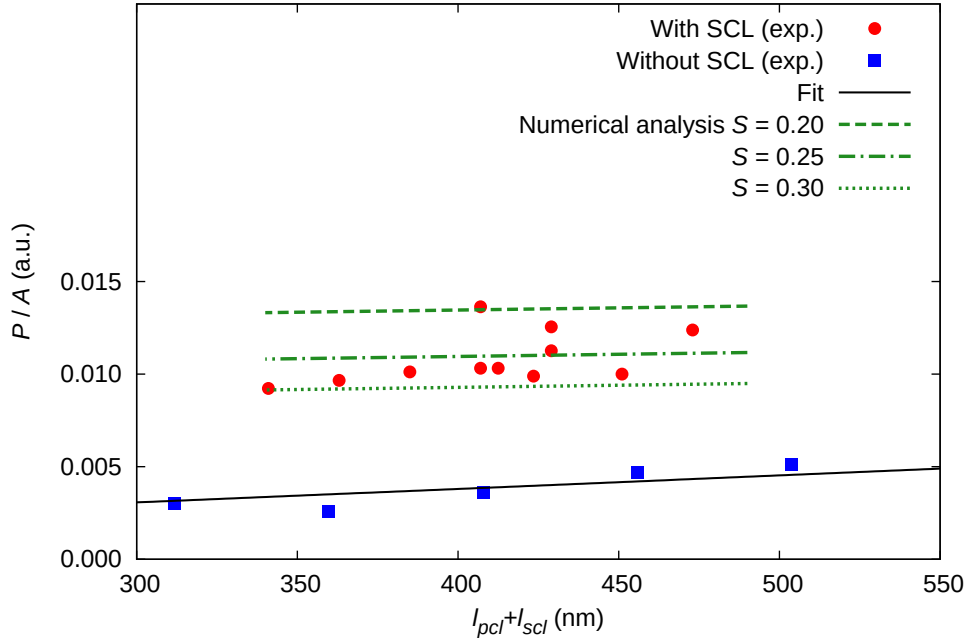


Figure 5.10: Photoacoustic amplitude, P , over optical absorption, A , as a function of the thickness of the dielectric layer, $l_{pcl} + l_{scl}$, at the laser modulation frequency of 60 kHz. The solid line is the fitting result of the theoretical solution for the samples without an SCL. The dashed lines are the results of the numerical analysis for the samples with an SCL, for the filling factors, $S = 0.20$, 0.25 , and 0.30 .

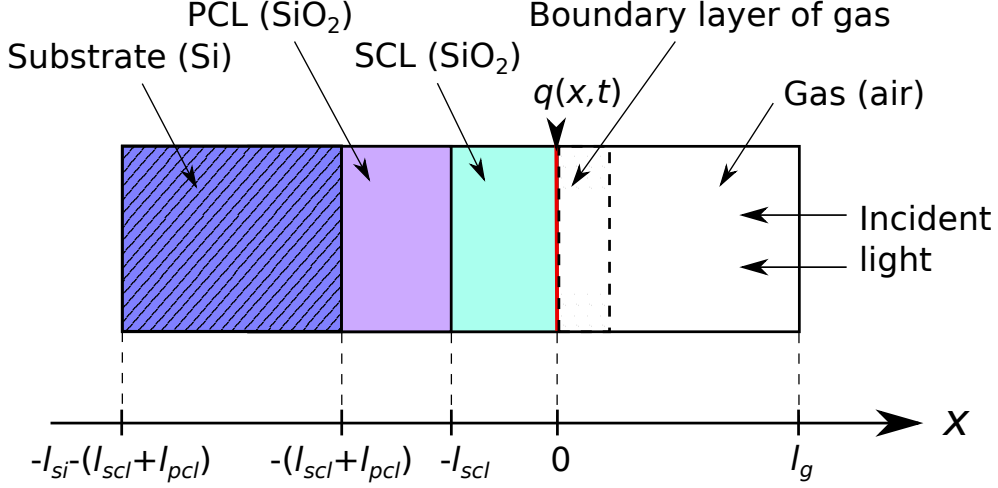


Figure 5.11: Schematic diagram of heat transfer model and the coordinate configuration.

5.2.3.2 One-Dimensional Heat Transfer Model

In order to clarify the contribution of the porosity and the thickness of the dielectric layer to the photoacoustic amplitude, we investigated the thermally induced acoustic emission from the local plasmon resonator with an SCL, on the basis of a one-dimensional heat transfer model, as depicted in Fig. 5.11. We assume that the system of the local plasmon resonator and the photoacoustic cell is composed of the Si, PCL, SCL, and gas (air) layers and that their thicknesses are l_{si} , l_{pcl} , l_{scl} , and l_g , respectively. Although the actual local plasmon resonators have the Ag mirror layer (200 nm) on the Si wafer, its thickness is significantly smaller than the thermal diffusion length of Ag and is negligible because of the uniformity of temperature inside the layer. In addition, we assume the Au NP layer at the top of the sample as a heat source whose thickness is negligibly small, because the thickness of the Au NP layer is significantly smaller than those of the other layers and the incident light is absorbed and converted into heat by the NP layer [10, 12]. This assumption is justified because the temperature inside Au NPs is expected to be uniform when excitation laser intensity is modulated at lower than 100 kHz, although there are several reports on pulsed laser excitation which causes inhomogeneous temperature distribution inside NPs [13, 14]. We define the sample surface to be at $x = 0$, and hence, the heat applied by the photothermal conversion is assumed to be

$$q(x, t) = AQ_0(1 + \cos \omega t) \delta(x), \quad (5.1)$$

where t is the time (s), Q_0 is the power density of the incident light (W m^{-2}), and ω is the laser modulation frequency (s^{-1}).

Assuming that there is no convection in the cell, the heat diffusion equation for each layer is written as

$$\frac{\partial u_i(x, t)}{\partial t} = a_i \frac{\partial^2 u_i(x, t)}{\partial x^2}. \quad (5.2)$$

Here, u_i is the temperature (K) and a_i is the thermal diffusivity ($\text{m}^2 \text{s}^{-1}$) defined by $a_i = \kappa_i / \rho_i C_i$, where κ_i , ρ_i , and C_i are the thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$), density (kg m^{-3}), and specific heat ($\text{J kg}^{-1} \text{K}^{-1}$) of the material i , respectively. The subscript i becomes si, scl, pcl, and g for the Si wafer, SCL, PCL, and gas (air), respectively. Equation (5.2) is solved under the boundary conditions that the temperature and heat-flux are continuous at interfaces. In addition, we assume that the temperature at the cell walls $x = l_g$ and $x = -l_{si} - (l_{scl} + l_{pcl})$ is the ambient temperature, T_0 .

The general solution for $u(0, t) \equiv u_{scl}(0, t) = u_g(0, t)$ can be written as

$$u(0, t) = U_{dc} + U_{ac} \cos(\omega t + \phi), \quad (5.3)$$

where U_{dc} and U_{ac} are complex-valued constants and ϕ is a real-valued constant for the phase factor. This periodic temperature change of the sample surface simultaneously causes expansion and contraction within a thin boundary layer of the gas next to the surface and produces acoustic pressure signals [1]. According to the derivation of Rosencwaig and Gersho [1], the photoacoustic amplitude can be written as

$$P = F \frac{|U_{ac}|}{|U_{dc}|}, \quad (5.4)$$

where F is a real-valued constant that can be determined by the shape of the photoacoustic cell and the property of the surrounding gas. In other words, F is essentially independent of the sample properties.

In order to obtain the value of F for our measurement system, we focus on the photoacoustic properties of the samples without an SCL that have a simple structure. For such samples,

$l_{scl} = 0$ and the analytical solution for Eq. (5.3) is written as

$$U_{dc} = T_0 + \frac{AQ_0 l_g (\kappa_{pcl} l_{si} + \kappa_{si} l_{pcl})}{\kappa_{pcl} \kappa_{si} l_g + \kappa_g (\kappa_{pcl} l_{si} + \kappa_{si} l_{pcl})}, \quad (5.5)$$

$$U_{ac} = \frac{AQ_0}{\kappa_{pcl} \sigma_{pcl}} \frac{(1-b) \exp(-\sigma_{pcl} l_{pcl}) + (1+b) \exp(\sigma_{pcl} l_{pcl})}{(1+c)(1+b) \exp(\sigma_{pcl} l_{pcl}) - (1-c)(1-b) \exp(-\sigma_{pcl} l_{pcl})}, \quad (5.6)$$

where

$$\sigma_i = (1+j) \left(\frac{\omega}{2a_i} \right)^{1/2}, b = \frac{\kappa_{si} \sigma_{si}}{\kappa_{pcl} \sigma_{pcl}}, c = \frac{\kappa_g \sigma_g}{\kappa_{pcl} \sigma_{pcl}}. \quad (5.7)$$

The real part of Eq. (5.6) represents the actual physical temperature variation. In the experiment, $T_0 = 2.9 \times 10^2$ K, $A < 1$, $Q_0 = 4.0 \times 10^4$ W m⁻², $\kappa_{si} = 1.5 \times 10^2$ W m⁻¹ K⁻¹, $\kappa_{pcl} = 1.4$ W m⁻¹ K⁻¹, $\kappa_g = 2.4 \times 10^{-2}$ W m⁻¹ K⁻¹, $l_{si} = 0.5 \times 10^3$ μm, and $l_g = 3.5 \times 10^3$ μm [8]. Therefore, the second term on the right-hand side of Eq. (5.5) is smaller than 1.4 K. Consequently, we can assume $|U_{dc}| \simeq T_0 = 290$ K. In Eqs. (5.6) and (5.7), $a_{pcl} = 6.2 \times 10^{-7}$ m² s⁻¹, $a_{si} = 9.0 \times 10^{-5}$ m² s⁻¹, and $a_g = 1.9 \times 10^{-5}$ m² s⁻¹. By substituting Eqs. (5.5)–(5.7) into Eq. (5.4), we obtain the photoacoustic amplitude of the local plasmon resonator without an SCL. Since the $|U_{dc}|$ in Eq. (5.5) is almost constant and $|\sigma_{pcl} l_{pcl}|$ in the Eq. (5.6) is small ($< 5 \times 10^{-7}$ s^{1/2}), the P is estimated to be almost independent of the dielectric thickness. The solid line shown in Fig. 5.10 shows the results of fitting the analytical solution to the experimental data, where F is the fitting parameter. We obtain the prefactor $F = 76 \pm 5$ from the fitting. The calculated data agrees well with the experimental data, which is almost independent of the dielectric thickness.

The value of F evaluated for the samples without an SCL was utilized to discuss the photoacoustic emission from the samples with an SCL. Since the samples with an SCL have many layers, it is difficult to derive an analytical solution for $|U_{ac}/U_{dc}|$ in Eq. (5.4). Thus, we performed a numerical calculation for the heat transfer model. Before performing the calculation, we needed to determine the SCL thermal diffusivity, a_{scl} , and the thermal conductivity, κ_{scl} . When we consider the one-dimensional energy balance of the volume element depicted in Fig. 5.5(b), κ_{scl} determines the heat flux in the direction normal to the interfaces, induced by the temperature gradient. As can be seen in the SEM image of the local plasmon resonator with an SCL (Fig. 5.6(a)), the SCL is composed of cylindrical SiO₂ columns growing along the surface

normal. Therefore, the filling factor, S , is equal to the area fraction of SiO_2 , as depicted in Fig. 5.5(b). The magnitudes of κ_{scl} and $\rho_{scl}C_{scl}$ are S times as large as those in the case of SiO_2 . Thus, the thermal diffusivity of the SCL, $a_{scl} = \kappa_{scl}/\rho_{scl}C_{scl}$, is equal to that of SiO_2 .

The results of the numerical analysis of the photoacoustic amplitude for $S = 0.20, 0.25$, and 0.30 are shown in Fig. 5.10. The calculation agrees with the experimental results when S is in the range of 0.25 – 0.30 . From the SEM images shown in Fig. 5.6 and in the previous paper [15], the filling factor of the SCL deposited at the deposition angle of $\sim 80^\circ$ is estimated to be in the range of 0.3 – 0.4 . This value is close to that determined in the present numerical analysis, even though the photoacoustic amplitude, P/A , exhibits high sensitivity to the filling factor, S . This result suggests that the photoacoustic amplitude is strongly dependent on the porosity of the SCL layer, which determines the thermal conductivity of the layer under the Au nanoparticles. By reducing the thermal conductivity of the underlying layer, the heat flux from the Au NPs to the substrate is decreased and that to the air is increased. Accordingly, the local temperature of the air is efficiently modulated and substantial photoacoustic emission is realized. Consequently, the low conductivity of the layer that contributes to the efficient photoacoustic emission is easily achieved by the DOD technique. Further improvement of the photoacoustic amplitude can be achieved by reducing the filling factor of the SCL layer or by utilizing materials with low thermal conductivity to form the layer.

5.2.4 Conclusion

We performed photoacoustic measurements on local plasmon resonators with Au NP layer/SCL (porous SiO_2 layer)/PCL/Ag mirror structures achieved by DOD. The photoacoustic amplitude of the local plasmon resonator with high absorption ($A = 0.95$) is eight times larger than that of graphite ($A = 0.94$) and three times larger than that of the sample without a porous SCL layer ($A = 0.93$). In addition, the signal from the local plasmon resonator with low absorption ($A = 0.03$) has the same order of magnitude as that from the highly reflective Ag thin film ($A = 0.01$). In order to verify the contribution of the porous SCL layer to the efficient photoacoustic emission, theoretical and numerical analyses based on the one-dimensional heat transfer model were performed. The results suggest that the low thermal conductivity of the porous SCL layer,

which is easily formed by DOD, contributes to the reduction of the amount of heat escaping to the substrate and to the efficient photoacoustic emission from Au NP arrays.

5.3 Enhancement of Photoacoustic Emission

5.3.1 Introduction

In Section 5.2, the photoacoustic emission was enhanced by a factor of 3 by inserting a 340-nm-thick porous SiO_2 layer having a thermal conductivity about 3–4 times lower than that of a planar SiO_2 layer. This result suggests that the reduction in the thermal conductivity of the layer supporting the Au NPs is critical to the enhancement of the photoacoustic emission. In this section, we propose two approaches to achieve further enhancement of the photoacoustic emission: (a) replacing the Si substrate with air and (b) introducing porous silicon.

In approach (a) (Section 5.3.2), we focus on the Si substrate underlying the local plasmon resonator and replace it with air, which has a thermal conductivity that is more than three orders of magnitude lower than that of Si [8]. We propose a method of fabricating self-supported local plasmon resonators and show their remarkable photoacoustic emission.

In approach (b) (Section 5.3.3), we focus on nanostructured porous silicon (nanoPS), which was used to enhance the thermally induced ultrasonic emission [9]. NanoPS, which has a thermal conductivity as low as that of the porous SiO_2 layer [16, 17], can be obtained without a vacuum process. Here, as a prototype, we investigate the photoacoustic emission from a Cu NP/nanoPS system, which can be prepared by electrochemical etching (nanoPS layer) and photoassisted electroless deposition (Cu NPs).

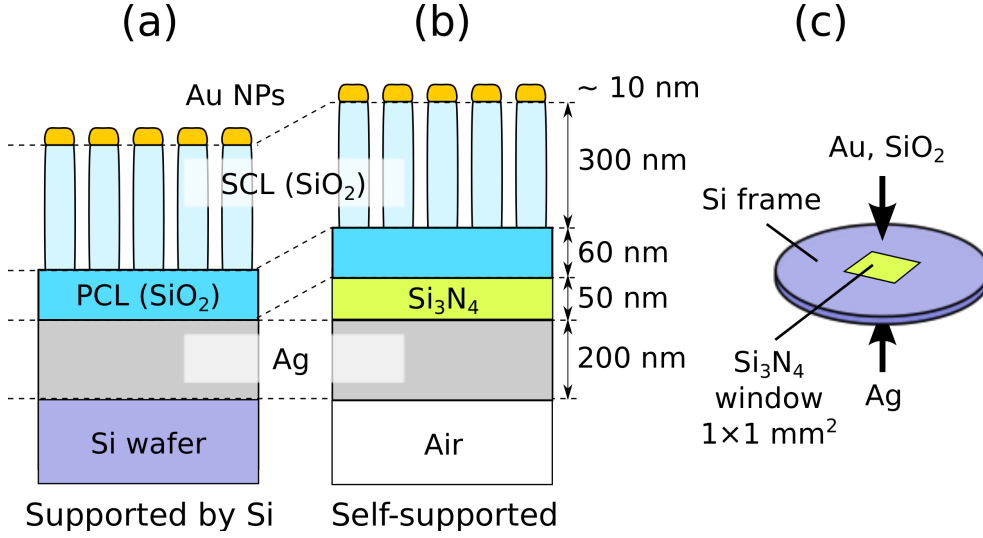


Figure 5.12: Schematic drawing of local plasmon resonators.

5.3.2 Approach (a): Self-Supported Local Plasmon Resonators

5.3.2.1 Experiments

In Chapter 3, we demonstrated the fabrication of local plasmon resonators supported by a Si wafer, as depicted in Fig. 5.12(a). Here, we propose a method of fabricating self-supported Au NP/SCL/PCL/Si₃N₄/Ag mirror structures (Fig. 5.12(b)), i.e., self-supported local plasmon resonators, by dynamical oblique deposition. We used a commercial silicon nitride membrane (50 nm thick, 1 mm square) and deposited thin films on both sides of it (Fig. 5.12(c)). First, a smooth Ag layer 200 nm in thickness was deposited on one side of the membrane. Then, on the other side of the membrane, a PCL of 60-nm-thick SiO₂ was deposited from the normal direction to the surface. On the PCL, an SCL of SiO₂ up to 300 nm thick was prepared. During SCL deposition, the deposition angle measured from the surface normal was fixed at 78.6°, and the substrate was rotated continuously and rapidly. As a result, SiO₂ nanopillars on the PCL were obtained. Finally, an Au NP layer 8.6 nm in thickness was deposited on the SCL at a deposition angle of 83.4°. We also fabricated local plasmon resonators supported by a Si wafer (Fig. 5.12(a)) using the fabrication method reported in Chapter 3.

Optical reflection measurements at an angle of incidence of 2° were conducted using a single-beam spectrophotometer in the wavelength range of 300 nm < λ < 1700 nm. Because the optical transmittance and scattering of our samples are negligibly small, their optical absorption A was

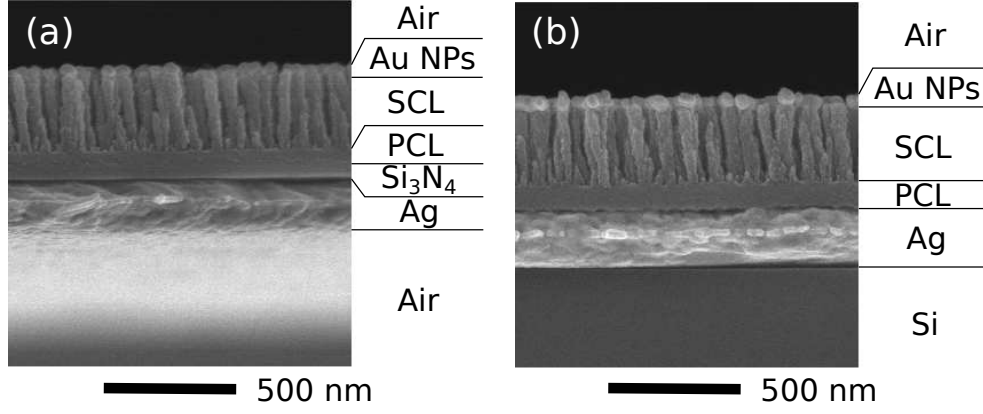


Figure 5.13: Typical cross-sectional SEM images of (a) self-supported local plasmon resonator and (b) resonator supported by air.

evaluated as $A = 1 - R$, where R is the optical reflectance.

The photoacoustic measurements [18] were performed using a photoacoustic cell (10.0 mm in diameter and 3.5 mm in height, Fig. 5.1) on the self-supported local plasmon resonators and, for comparison, on those supported by a Si wafer. We loaded the sample, which has an area of $1 \text{ mm} \times 1 \text{ mm}$, onto the photoacoustic cell filled with air. Then, the sample was irradiated by a laser (wavelength 785 nm), the intensity of which was modulated sinusoidally. The angle of incidence of the laser was perpendicular to the sample surface. The photoacoustic signal detected by a microphone was measured with a lock-in amplifier and recorded as a function of the laser modulation frequency over a range of 1 kHz to 100 kHz.

5.3.2.2 Results and Discussion

Figure 5.13 shows typical cross-sectional SEM images of (a) the self-supported sample and (b) the sample supported by the Si wafer. The self-supported sample (Fig. 5.13(a)) is held by the smooth 50-nm-thick Si_3N_4 membrane, which can be found between the Ag and the PCL. Because the SEM image of the self-supported sample was taken from a slightly tilted angle with respect to the sample surface, the lower surface of the Ag layer, which appears to be glowing white, is visible. These SEM observations suggest that the self-supported local plasmon resonators with the Au NP/SCL/dielectric spacer/Ag mirror layer structure depicted in Fig. 5.12(b) were successfully fabricated as intended by dynamical oblique deposition.

Figure 5.14 shows typical optical absorption spectra of the self-supported sample (red solid

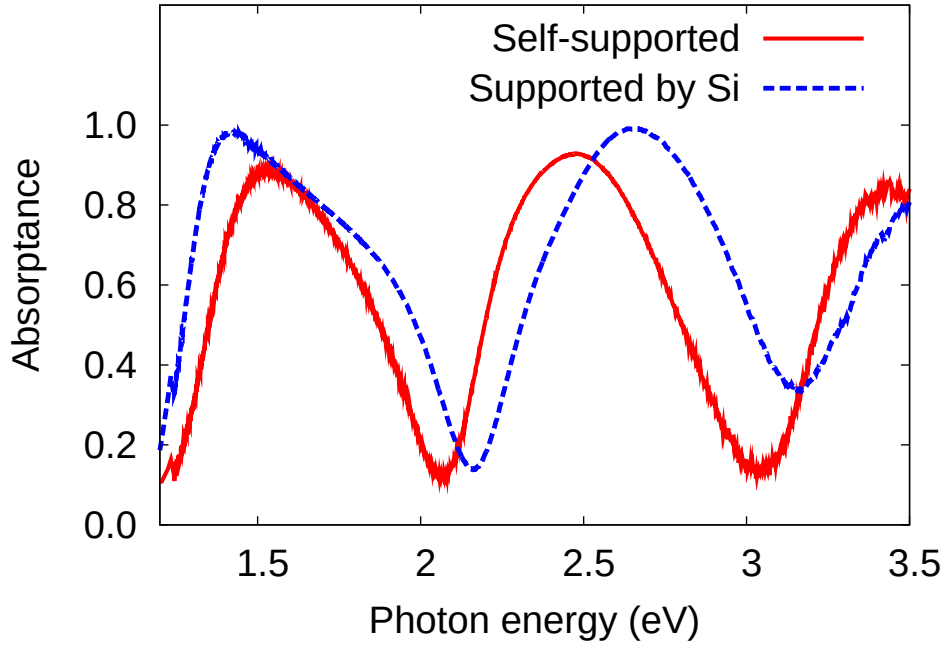


Figure 5.14: Optical absorption spectra of self-supported local plasmon resonator (red solid line) and resonator supported by Si wafer (blue dashed line).

line) and the sample supported by a Si wafer (blue dashed line). The sample supported by a Si wafer (blue dashed line) shows a periodic change in its optical absorption as a function of the photon energy due to interference, which is a typical spectral feature of local plasmon resonators [10, 19]. Their optical properties can be understood in terms of multiple homogeneous layers, at least around the near-infrared or longer-wavelength region, because the dimensions of the nanostructures in the layers are much smaller than the wavelength (see Chapter 2). Although the self-supported sample has an additional Si_3N_4 layer in the dielectric layers of the local plasmon resonator, it shows spectral features similar to those of the sample supported by a Si wafer. This result suggests that the presence of the Si_3N_4 layer affects only the phase of the interference, and optically equivalent structures were successfully fabricated on both Si and air substrates. Among the fabricated samples, the two depicted in Fig. 5.14 showed almost the same optical absorption at a wavelength of 785 nm (1.58 eV). These samples are suitable for investigating the contribution of the thermal properties of the substrate to the photoacoustic emission from the local plasmon resonators. Therefore, we performed photoacoustic measurements on those samples using a 785-nm-wavelength laser and compared their photoacoustic emission.

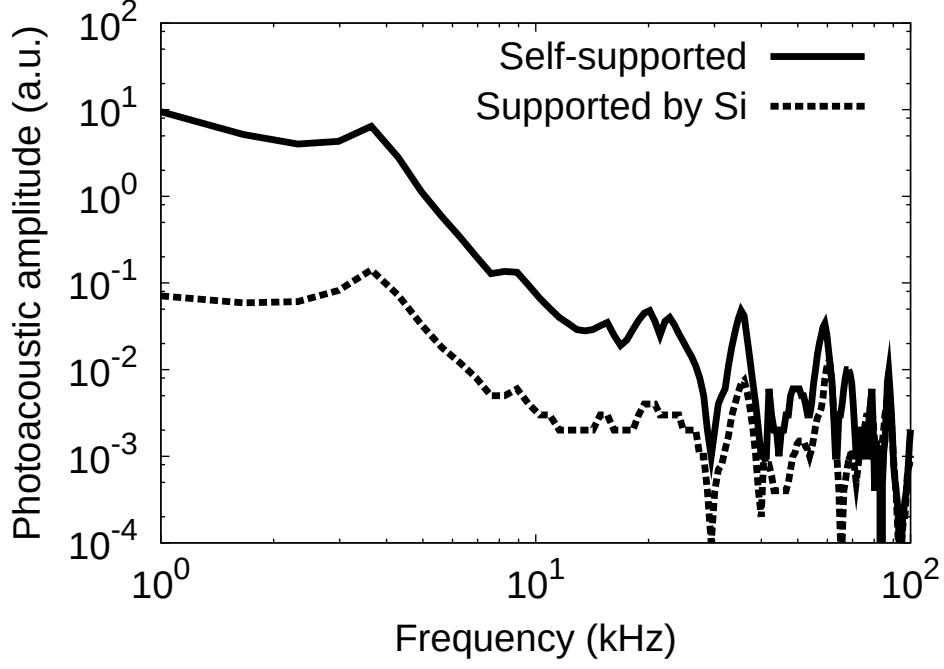


Figure 5.15: Photoacoustic spectra of self-supported local plasmon resonator (solid line) and resonator supported by Si wafer (dashed line).

Figure 5.15 shows the photoacoustic spectra of the self-supported sample (solid line) and the sample supported by a Si wafer (dashed line) as a function of the laser modulation frequency. These spectra have many distinct peaks at identical positions. The peaks originate in the acoustic resonance in the photoacoustic cell. Apart from these resonance peaks, we focused our attention on the relative amplitudes of the obtained spectra, which qualitatively describe the surface temperature modulation of the samples [1]. Although the self-supported sample and the sample supported by a Si wafer exhibit almost the same optical absorption, the photoacoustic amplitude P of the self-supported sample is more than 2 orders of magnitude larger than that of the sample supported by a Si wafer at a laser modulation frequency of 1 kHz. This result suggests that the photoacoustic amplitude of the Au NP array is significantly improved by replacing the Si substrate with air, which has a thermal conductivity about 3 orders of magnitude lower than that of a Si wafer [8].

5.3.2.3 Numerical Analysis

To quantitatively compare the photoacoustic amplitude of the self-supported sample, P_{air} , and that of the sample supported by a Si wafer, P_{si} , we plotted P_{air}/P_{si} as a function of the laser

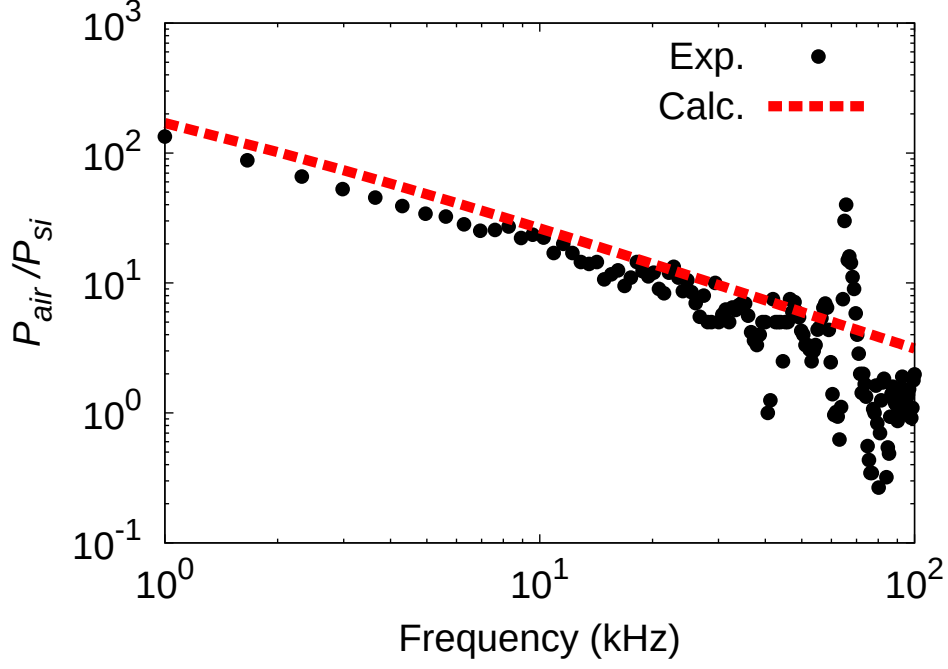


Figure 5.16: Ratio of the photoacoustic amplitudes of self-supported sample and sample supported by Si wafer, P_{air}/P_{si} , as a function of laser modulation frequency (black dots). Red dashed line shows the calculation result.

modulation frequency (Fig. 5.16, black dots). The value of P_{air}/P_{si} increased rapidly with decreasing laser modulation frequency. This frequency characteristic of P_{air}/P_{si} is expected to be understood by heat transfer analysis because the photoacoustic amplitude is known to arise from the periodic temperature change of the sample surface [1]. Therefore, we evaluated P_{air}/P_{si} using a one-dimensional heat transfer model, the procedure for which is essentially the same as that shown in Paragraph 5.2.3.2.

According to the derivation of Rosencwaig and Gersho [1], the relationship between the sample surface temperature and the photoacoustic amplitude can be written as

$$P = F \frac{|U^{ac}|}{|U^{dc}|}, \quad (5.8)$$

where U^{ac} and U^{dc} are the AC and DC components of the sample surface temperature, respectively, and F is a constant that is determined by the shape of the photoacoustic cell and the physical properties of the surrounding gas. Because the laser irradiation power is not very strong, and U^{dc} is estimated to be about room temperature [18], we can assume $P_{air}/P_{si} = |U_{air}^{ac}| / |U_{si}^{ac}|$, where the subscripts “air” and “si” represent the self-supported

Table 5.4: Thermal conductivity κ and thermal diffusivity a of each layer.

Materials	Air [8]	PCL [20]	SCL [18]	Si ₃ N ₄ [21]	Si [8]
κ (W m ⁻¹ K ⁻¹)	2.4×10^{-2}	8.0×10^{-1}	2.0×10^{-1}	2.7×10^0	1.5×10^2
a (m ² s ⁻¹)	1.85×10^{-5}	3.70×10^{-7}	3.70×10^{-7}	1.24×10^{-6}	8.95×10^{-5}

sample, which has an air substrate, and the sample supported by a Si wafer, respectively. The value of $|U_{si}^{ac}|$ and $|U_{air}^{ac}|$ can be estimated by numerical calculation using a one-dimensional thermal diffusion equation if the thickness, thermal conductivity, and thermal diffusivity of each layer are defined.

Here, we assume that the systems of the self-supported local plasmon resonator and the resonator supported by a Si wafer in the photoacoustic cell are composed of air (500 μ m)/SCL (300 nm)/PCL (60 nm)/Si₃N₄ (50 nm)/air (500 μ m) and air (500 μ m)/SCL (300 nm)/PCL (60 nm)/Si (500 μ m), respectively. To eliminate the effect of the cell walls on the calculations, the air layer and Si layer are taken to be much thicker than their thermal diffusion length at 1 kHz, which is expressed by $\lambda = \sqrt{a/\pi f}$, where a is the thermal diffusivity (m² s⁻¹), and f is the laser modulation frequency (s⁻¹). The thermal conductivity and diffusivity of the layers are listed in the Table 5.4. For the PCL (SiO₂) and Si₃N₄ layer, we used the values of those thin films from the literature [20, 21]. The Si and air layers were considered as bulk layers, the thermal properties of which are given in the literature [8]. In addition, the thermal properties of the SCL, which can be treated as a homogeneous layer with a thermal conductivity 4 times lower than that of the PCL, were described in our previous paper [18]. Although the actual local plasmon resonators have a Ag mirror layer (200 nm) on the Si wafer, its thickness is significantly smaller than the thermal diffusion length of Ag and is negligible because of the uniformity of the temperature inside the layer. Furthermore, we assume that the Au NP layer at the top of the sample is a heat source whose thickness is negligibly small because the thickness of the Au NP layer is significantly smaller than those of the other layers, and the incident light is absorbed and converted into heat by the NP layer [18, 19]. We define the sample surface to be at $x = 0$; hence, the heat applied by photothermal conversion is assumed to be

$$q(x, t) = AQ_0(1 + \cos 2\pi ft)\delta(x), \quad (5.9)$$

where t is the time (s), and Q_0 is the power density of the incident light (W m^{-2}). Because, as described earlier, U_{dc} for the sample surface is estimated to be about room temperature, and also the amplitude of U_{ac} is sufficiently small, we can assume that air convection in the cell, which is caused by the temperature gradient, is negligibly small. Therefore, the heat diffusion equation for each layer is written as

$$\frac{\partial u(x, t)}{\partial t} = a \frac{\partial^2 u(x, t)}{\partial x^2}, \quad (5.10)$$

where u is the temperature (K). Equation (5.10) is solved under the boundary conditions that the temperature and heat flux are continuous at interfaces. In addition, we assume that the temperature at the cell walls, which are far from the heat source, is room temperature.

The red dashed line in Fig. 5.16 is the calculation result, which agrees well with the experimental result, shown by black dots. This result suggests that reducing the thermal conductivity of the substrate by replacing the Si wafer with air contributes to the enhancement of the photoacoustic emission. At a laser modulation frequency of 1 kHz, the thermal diffusion lengths of the PCL ($\lambda \simeq 10.8 \mu\text{m}$), SCL ($\lambda \simeq 10.8 \mu\text{m}$), and Si_3N_4 ($\lambda \simeq 19.9 \mu\text{m}$) are much greater than the thickness of the local plasmon resonators composed of those materials. Consequently, the thermal properties of the substrate, i.e., Si or air, under the multilayered thin film dominate the photoacoustic amplitude, and the reduction of the thermal conductivity has a pronounced effect on it.

5.3.2.4 Summary

The fabrication of self-supported local plasmon resonators and their photoacoustic emission are demonstrated. Using silicon nitride membranes, self-supported Au NP/PCL/SCL/ Si_3N_4 /Ag structures are successfully fabricated. At a laser modulation frequency of 1 kHz, the photoacoustic amplitude of the self-supported sample is more than 2 orders of magnitude larger than that of the sample supported by a Si wafer. This large enhancement of the photoacoustic emission is due to a reduction in the thermal conductivity of the substrate caused by replacing the Si wafer with air, which is verified using a one-dimensional heat transfer model. In addition, the thermal diffusion length becomes much longer than the thickness of the local plasmon res-

onators at a laser modulation frequency of 1 kHz, so the photoacoustic emission significantly reflects the change in the thermal properties of the substrate. Consequently, the self-supported local plasmon resonators are suitable for use as sound-emitting devices in the audible frequency range.

5.3.3 Approach (b): Photoacoustic Emission from Cu NPs/nanoPS

5.3.3.1 Experiments

The Cu NP/nanoPS structures were prepared as follows: The nanoPS layers were fabricated by electrochemical etching of boron-doped p⁺-type silicon wafers (resistivity 0.01 to 0.05 Ω cm; orientation <100>). The composition of the solution was 1:2 hydrofluoric acid (48 wt.%):ethanol (98 wt.%). The wafers were galvanostatically etched under illumination from a 100 W halogen lamp. An etching density current of 80 mA cm⁻² was applied for 20 s to grow layers around 75% in porosity and 750 nm in thickness. Cu NPs were deposited over the p⁺-type crystalline Si and nanoPS layers by immersing the substrates in CuSO₄ (50 mM) and H₂SO₄ (1 mM) aqueous solutions at room temperature for different durations. H₂SO₄ was used to stabilize the pH. Deposition was activated by turning on the 100 W halogen lamp during the appropriate time. Once deposition was finished, the samples were washed and rinsed twice in water and twice in ethanol and subsequently dried with N₂. Field emission scanning electron microscopy (FESEM) images of those samples were acquired to evaluate their morphologies. Optical characterization was performed using a Jasco V-560 UV-vis spectrophotometer (Halifax) equipped with a Hamamatsu R928 photomultiplier (Hamamatsu Photonics, Iwata). All measurements were taken in the wavelength range between 350 and 850 nm with a 1 nm interval and 1 s integration time.

5.3.3.2 Results and Discussion

The surface of a typical fresh nanoPS layer is shown in Fig. 5.17(a). A porous structure with an average pore size of around 40 nm is clearly observed. After the nanoPS layer was immersed in copper solutions under illumination for 60 s, copper NPs were nucleated on the surface, as depicted in Fig. 5.17(b). This figure shows that the Cu NPs have a pseudo-spherical shape and wide size distribution, with a maximum around a diameter of 100 nm. Figure 5.17(c) shows a cross section of a nanoPS layer after Cu electroless deposition. This figure shows a typical longitudinal porous structure; the thickness of the nanoPS layer is around 750 nm. In

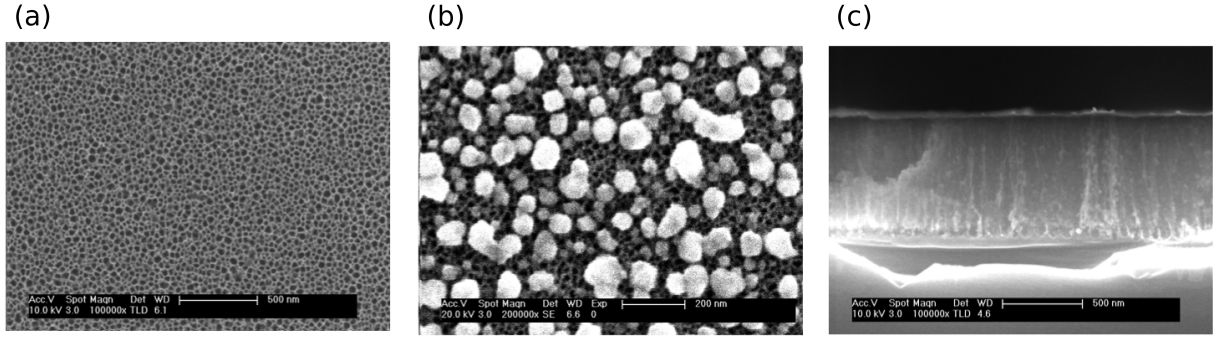


Figure 5.17: FESEM images. Fresh nanoPS surface (a) before and (b) after immersion in the Cu solution, and (c) cross section after immersion in the solution.

addition, some copper NPs can be observed inside the porous structure, demonstrating that Cu deposition occurs not only over the PS surface but also inside the pores.

Figure 5.18 shows the photoacoustic spectra of nanoPS covered by Cu NPs (nanoPS+Cu), bare nanoPS, a Si wafer covered by Cu NPs (Si+Cu), and a bare Si wafer. These spectra have many distinct peaks at identical positions, which originate from acoustic resonance in the experimental photoacoustic cell. Apart from these resonance peaks, we focused on the relative amplitudes of the obtained spectra. The photoacoustic response of a crystalline Si wafer increased slightly when copper NPs were deposited on the surface, although the absorption at 785 nm is quite similar for both samples.

On the other hand, the photoacoustic response of the nanoPS layer is about two times higher than that of c-Si. This increase is due mainly to the lower thermal conductivity and higher light absorption of the nanoPS layers. When Cu NPs are deposited on nanoPS, the photoacoustic response increases significantly, although the absorption at 785 nm is quite similar. This increase can be attributed to the Cu NPs acting as localized heat sources near the surface, where heat exchange between the Cu NPs and air is more efficient, increasing the total temperature of the devices and therefore the photoacoustic intensity.

To evaluate the enhancement of the photoacoustic response, we compared the photoacoustic spectra of nanoPS+Cu ($A = 0.94$) and local plasmon resonators ($A = 0.93\text{--}0.95$), all of which have high optical absorption A at a wavelength of 785 nm (Fig. 5.19). The local plasmon resonators have Au NP/dielectric/Ag mirror structures that can be prepared using the DOD technique (see Chapter 3). Because of strong interference, their light absorption is highly

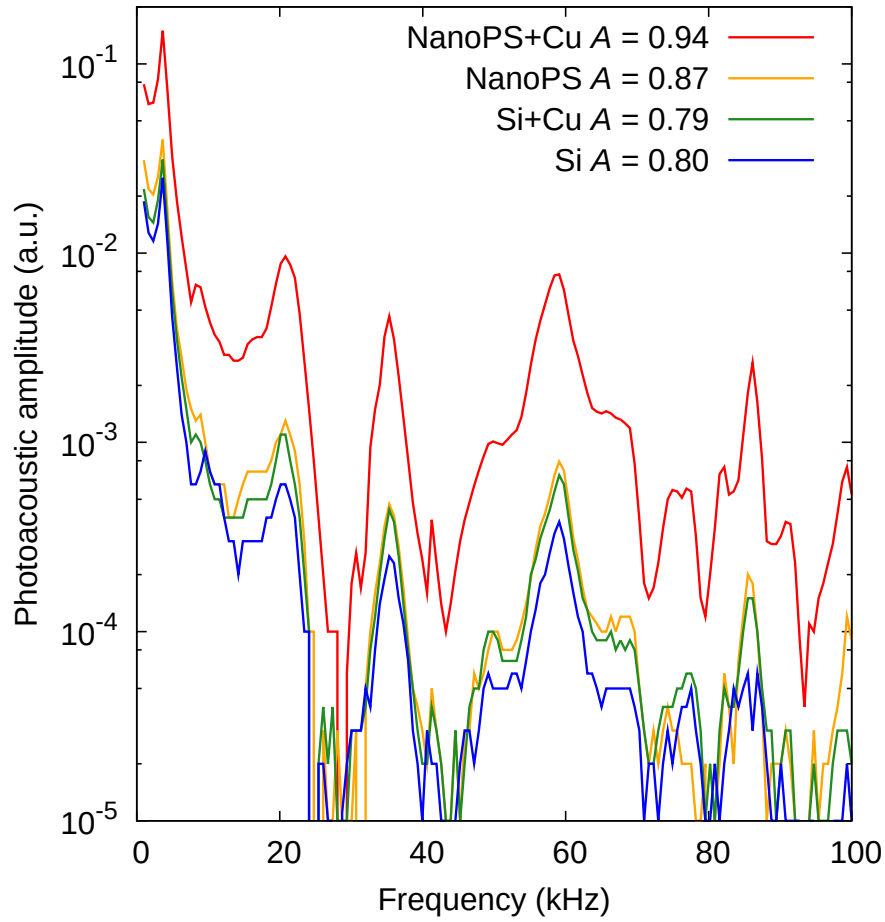


Figure 5.18: Photoacoustic spectra of Si wafer (Si), Si wafer after immersion in the Cu solution (Si+Cu), nanoPS layer (nanoPS), and nanoPS layer after Cu NP deposition (nanoPS+Cu). Photoacoustic measurements were performed with a 785-nm-wavelength laser.

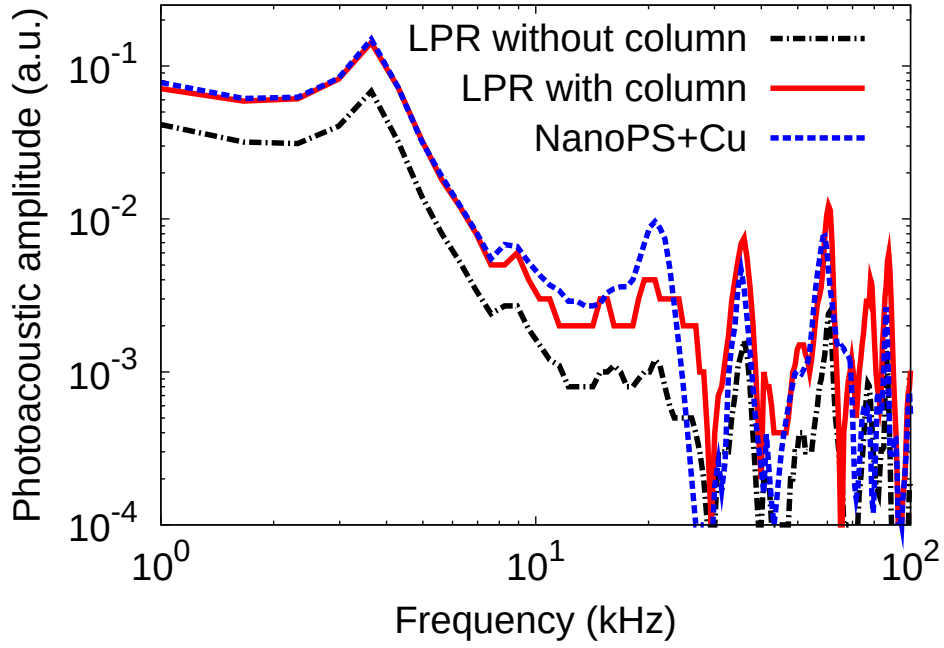


Figure 5.19: Photoacoustic response of nanoPS+Cu and local plasmon resonators (LPRs) with and without a porous column layer.

localized in the Au NP layer, which enhances the periodic temperature change of the sample surface and simultaneously contributes to the emission of a strong photoacoustic response compared to bulk absorbers such as graphite (see Section 5.1). The local plasmon resonator whose dielectric layer consists of porous SiO₂ column layers (Fig. 5.19, red line) has been shown to generate a 2–3 times larger photoacoustic response than that whose dielectric layer consists of a solid SiO₂ layer (Fig. 5.19, black line) [19], whereas the photoacoustic response from nanoPS+Cu is almost the same as that from the local plasmon resonator with a column layer. This enhancement is related to the low thermal conductivity of the porous column layer and nanoPS layer, which contributes to the reduction in the amount of heat escaping to the substrate and to the efficient photoacoustic emission from metal NP arrays.

To verify the contribution of the porous column and nanoPS layers to the efficient photoacoustic emission, numerical analyses based on the one-dimensional heat transfer model were performed [19]. The calculation method is basically the same as that shown in Paragraph 5.2.3.2. In the heat transfer model for the nanoPS+Cu, we assumed that the Cu NPs layer on the sample surface is the localized heat source. As already shown in Section 5.2, the enhancement ratio, P_c/P_{SiO_2} , where P_c and P_{SiO_2} represent the photoacoustic response of a local plasmon

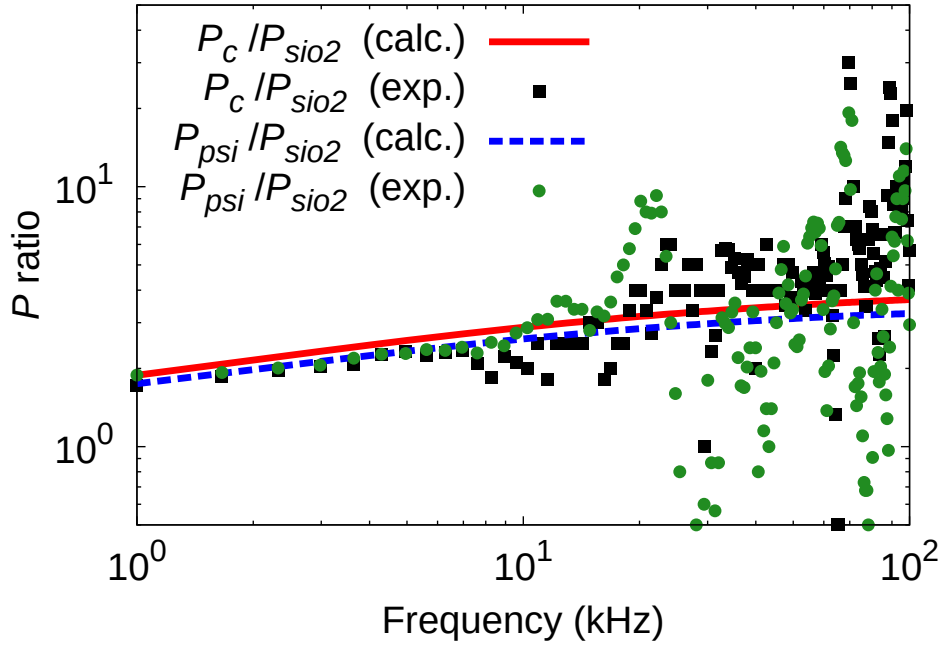


Figure 5.20: Ratio of photoacoustic responses P_c/P_{sio2} (black squares) and P_{psi}/P_{sio2} (green circles) as a function of laser modulation frequency. P_c , P_{sio2} , and P_{psi} represent the photoacoustic response of local plasmon resonators with and without a porous column layer and that of nanoPS+Cu, respectively. Red and blue dashed lines show the calculation results for P_c/P_{sio2} and P_{psi}/P_{sio2} , respectively.

resonator with and without a porous column layer, respectively, agrees well with the experimental results (black squares in Fig. 5.19). This suggests that the photoacoustic enhancement originates in the existence of the porous column layer with low thermal conductivity. On the other hand, the thermal conductivity of the nanoPS layer under Cu NPs (approximately $0.6 \text{ W m}^{-1} \text{ K}^{-1}$) [16] is of the same order of magnitude as that of the porous column layer (approximately $0.2 \text{ W m}^{-1} \text{ K}^{-1}$) [17], and it is expected to act as a thermal insulation layer, like the porous column layer. In fact, the calculated P_{psi}/P_{sio2} , where P_{psi} represents the photoacoustic amplitude of nanoPS+Cu, agrees well with the experimental results, suggesting that the strong photoacoustic emission from nanoPS+Cu can be understood well in terms of the low thermal conductivity of the nanoPS layer. Consequently, we can conclude that hybrid systems composed of nanoPS and noble metal NPs can be used for thermoplasmonic applications; further, they have much simpler structures than the local plasmon resonator and can be fabricated without a vacuum system.

5.3.3.3 Summary

The photoacoustic emission from nanostructured copper/porous silicon hybrid systems was studied to investigate the possibility of introducing a new material into local plasmon resonators. Copper NPs were grown by photoassisted electroless deposition on crystalline silicon and nanoPS. The experimental results show a remarkable increase in the photoacoustic intensity when copper NPs are incorporated into the porous structure. The photoacoustic emission from a Cu/nanoPS hybrid system was compared with that from the local plasmon resonators and evaluated using the one-dimensional heat transfer model. The calculation results suggest that the low thermal conductivity of the porous silicon contributes to the photoacoustic enhancement, as expected. The results thus suggest that Cu/nanoPS hybrid systems are suitable candidates for several applications in the field of thermoplasmonics, including the development of highly efficient sound-emitting devices. In addition, porous silicon is promising for application as a component of local plasmon resonators.

5.4 Conclusion

In this chapter, the temporal controllability of photothermal conversion in local plasmon resonators was investigated experimentally and theoretically using the photoacoustic effect. The following outcomes suggest that local plasmon resonators are suitable for temporal control of photothermal conversion and demonstrate their applicability as nanoheaters for microfluidic control using photoacoustic generation and thermophoresis, as well as in sound-emitting devices:

- The photothermal conversion in local plasmon resonators is highly localized in the thin Au NP layer (~ 10 nm), which enables rapid modulation of the temperature of the surrounding fluid compared to bulk absorbing materials.
- The low thermal conductivity of the porous SCL layer, which is easily formed by DOD, contributes to the reduction in the amount of heat escaping to the substrate and to the efficient photoacoustic emission from Au NP arrays.
- The photoacoustic emission is further enhanced by reducing the thermal conductivity of the sample by the following methods: (a) replacing the Si substrate with air and (b) introducing porous silicon.

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Chapter 6

Application of Local Plasmon Resonators: Microfluidic Control

6.1 Introduction

In the last 4 chapters, optical and photothermal conversion properties of local plasmon resonators have been discussed. The intent of this chapter is to present one of the applications of their photothermal conversion and to show their potential as a microheater.

Temperature gradient along a gas-liquid interface causes surface tension differential along the surface, which results in a liquid motion. This phenomenon has long been known as the Marangoni or thermocapillary effect [1, 2]. Fluid manipulation mediated by this Marangoni effect has been investigated numerically [3–6] and experimentally [7–13] and its potential for microfluidic control has been shown. Especially, a small bubble of the order of 10 μm was shown to be capable of developing a jet like Marangoni flow with a high velocity of more than 100 mm/s using a thin wire heater of 0.1 mm diameter [10]. If we can manipulate this strong flow in a micro channel, it could be a novel and powerful driving force in microfluidics. A key issue in manipulating the Marangoni flow around a micro bubble is the difficulty of controlling the temperature gradient at a micrometer scale flexibly and precisely.

A remarkable feature of the local plasmon resonators is strong and highly localized optical absorption in the Au NP layer (~ 0.97) [14] (see Chapter 2). This feature allows them to convert

almost all of the incident light to heat within the thin surface layer (~ 10 nm). Taking advantage of their localized photothermal conversion, we demonstrate that their strong photoacoustic emission is eight times larger than that of a graphite which has a high optical absorption of 0.85 [14] (see Chapter 5). Another feature that makes the local plasmon resonators attractive as a heater is the existence of a layer of SiO_2 nanocolumns under the Au NPs. In our previous work, the photoacoustic emission was enhanced by a factor of three by inserting a 340-nm-thick porous SiO_2 nanocolumn layer whose thermal conductivity was about 3–4 times lower than that of a plane SiO_2 layer (see Chapter 5). This result suggests that the SiO_2 nanocolumn layer reduces in-plane and out-of-plane heat transfer from Au NPs to the substrate. Accordingly, the generated heat is highly localized under the spot of the irradiated light. In other words, a focused light on the local plasmon resonator can be used as a localized and mobile point-heat-source at the micrometer scale.

Some researchers have recently demonstrated using photothermal conversion to control the Marangoni flow around micro bubbles [15–21]. However, there are only a few studies that have observed the detailed dependence of the Marangoni flow on the relative position of the bubble and the laser spot, i.e. the heat source. In this chapter, we demonstrate drastic transformation of the Marangoni flow around a micro bubble by controlling the heating position at a micrometer scale using a well-localized photothermal conversion of the local plasmon resonator. In addition, we propose a size-based particle sorting method as an application of the controlled Marangoni flow around a micro bubble.

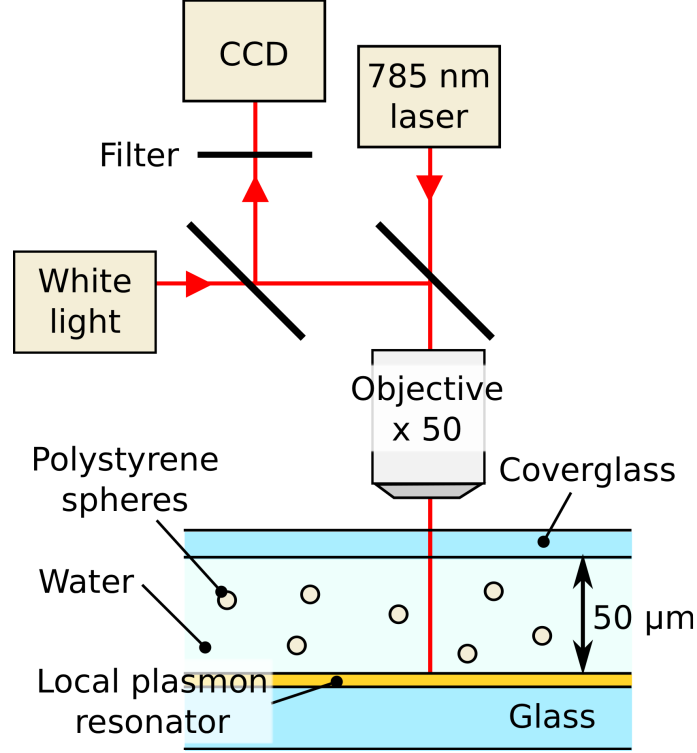


Figure 6.1: Schematic of the experimental setup used in the study.

6.2 Experiments

We prepared the local plasmon resonators with Au NP/SiO₂ nanocolumns/SiO₂/Ag structures by using DOD. Their preparation method is essentially the same as that reported in prior publications and Chapter 3 [14, 22, 23]. First, a smooth Ag layer (200 nm) and a SiO₂ layer (60 nm) were deposited on a glass substrate. On the SiO₂ layer, a 300 nm thick SiO₂ nanocolumn layer was prepared. During the deposition of the nanocolumns, the deposition angle measured from the surface normal was fixed at 80°, and the substrate was continuously and rapidly rotated. A Au NP layer (~ 8.5 nm) was then deposited at a deposition angle of 73.4° on the nanocolumns. The optical reflection of the sample in water was measured at an incidence angle of 2° using a single-beam spectrophotometer. Finally, we obtained local plasmon resonators with high optical absorption of 89% in water at the wavelength of 785 nm, at which we performed photothermal conversion.

Figure 6.1 shows a schematic of experimental setup for microfluidic control. A shallow cell, of 50-μm height, was created on the local plasmon resonator and filled with water in which polystyrene spheres (R0200, Thermo Scientific) with a diameter of 2 μm were dispersed.

Although these polystyrene spheres are necessary to visualize the fluid motion, their water suspension often contains a surfactant that considerably weakens the surface tension. Therefore, we carefully chose a water suspension of polystyrene spheres containing only a small amount of surfactant and diluted it with distilled water to a ratio of 1:20 (particle number density: $\sim 1 \times 10^8 \text{ cm}^{-3}$). The prepared sample cell was observed using an objective lens (50x, NA = 0.42) in an upright microscope (M-scope, Synos) under white light illumination. The objective lens was also utilized to focus the laser for photothermal conversion on the local plasmon resonator. The diameter of the laser spot was less than $10 \text{ }\mu\text{m}$ and the laser power at the sample surface was tunable from 0 mW to 13.5 mW. Fluid motion visualized by the motion of polystyrene spheres was recorded by a CCD (DMK 41AU02, The Imaging Source), whose exposure time was set at 5 ms. A short-pass filter was placed in front of the CCD to eliminate the 785-nm laser source.

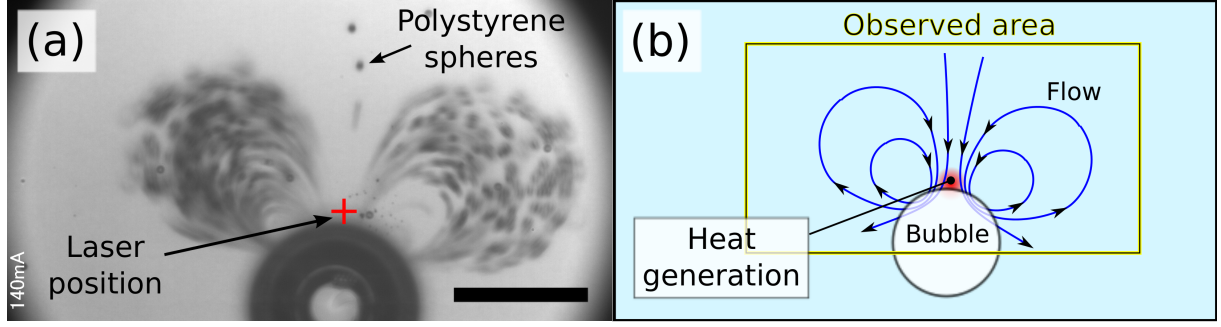


Figure 6.2: (a) Microscopic image of the rapid flow around the micro bubble induced by the photothermal conversion of the local plasmon resonator. The red crosses show the laser position, the small black dots are the polystyrene spheres, and the big black circle is the micro bubble with a diameter of $\sim 65 \mu\text{m}$, respectively. Scale bar: $50 \mu\text{m}$. (b) Sketch of the flow around the bubble.

6.3 Results and Discussion

6.3.1 Microfluidic Flow around a Micro Bubble

With the laser at the maximum power of 13.5 mW focused on the local plasmon resonator, a micro bubble with a diameter of $40\text{--}50 \mu\text{m}$ was generated because of the highly localized photothermal conversion. The laser power was tuned down to 12 mW and the irradiated spot moved to a position near the created bubble. When the laser position was set next to the bubble, a unique and rapid flow developed around the bubble. Figure 6.2 (a) shows an optical image of the typical flow around the bubble, whose motion is described in Fig. 6.2 (b). The flow pattern basically consists of a strong main flow towards the bubble and two symmetric rotation flows on either side of it. The velocity of the flow is at least of the order of mm s^{-1} since the images of the polystyrene spheres are elongated in the direction of the flow (see Section 6.3.2). We assert that this rapid flow is driven by the Marangoni effect because of the following reasons. Due to the localized photothermal conversion of the local plasmon resonator, a portion of the bubble surface near the laser spot is heated up. The surface tension of the heated point is significantly weakened and generates a strong shear force along the bubble surface that drags the surrounding fluid and induces rapid flow. Here, we provide a rough estimation of this Marangoni effect. When the temperature varies along the bubble surface from T_h at the hot pole near the laser spot to T_c at the cold pole, the average shear force on the bubble surface is given by $\bar{\tau} = (\sigma(T_c) - \sigma(T_h))/\pi r$. In this equation, $\sigma(T)$ is the surface tension of water at

temperature T and r is the radius of the bubble. If the fluid was simply a Newtonian fluid with constant viscosity, μ , the balance of the viscous stress and the shear force is given by $\bar{\tau} = \mu \nabla v$, where ∇v is the gradient of the flow velocity around the bubble. Assuming that the flow velocity is zero on the cell wall, we have $\nabla v \simeq v_p/h$, where v_p is velocity of the observed PS spheres and h is the distance between those PS spheres and the cell wall. In our experimental conditions, $h \simeq 2 \mu\text{m}$ because the observed PS spheres were distributed $\sim 2 \mu\text{m}$ above the bottom surface of the cell considering the depth of focus. In addition, $r \simeq 30 \mu\text{m}$ and v_p was at least 10–20 mm/s near the bubble surface. The values of μ and $\sigma(T)$ of water at around room temperature can be found in the literature. [24, 25] By using the equations above, the temperature gradient along the bubble surface is estimated to be $\nabla T = T_h - T_c \simeq 5 \text{ K}$ around room temperature. This result suggests that it is reasonable to classify the observed rapid flow as Marangoni flow. A more precise analysis would require the determination of the temperature distribution around the bubble at a micrometer scale. Instead, we investigated qualitative changes in the developed flow around the bubble by systematically varying the relative position of the laser spot and the bubble because the Marangoni effect is known to be very sensitive to the temperature gradient.

Figure 6.3 shows the transformation of the flow around the micro bubble at different positions of the laser spot. Please note that all these images were obtained by a sequence of observations on the same bubble. When the laser spot was located at or near the center of the bubble, there was no distinct flow (Fig. 6.3 (a)). However, when the laser position was moved slightly away from the center (Fig. 6.3 (b)), a rapid flow was suddenly observed to develop. This flow also consists of a strong main flow towards the bubble and two symmetric rotation flows with a distinct appearance change from that of Fig. 6.2 (a). In Fig. 6.3 (a), the rotation flow drives and mixes the polystyrene spheres rather than trapping them. As the laser position is gradually moved away from the bubble center (Figs. 6.3 (c)–(e)), the shape of the rotation flow undergoes a significant transformation. The distinguishing characteristic of the rotation flow was observed at the laser position of Figs. 6.3 (c) and (d), where the polystyrene spheres are tidily ranged in two symmetric circular shapes. The radius of the circle was tunable by the laser position. Just before the laser moved out from the bubble (Fig. 6.3 (f)), there was a region where the polystyrene spheres could not be driven. When the laser spot was moved

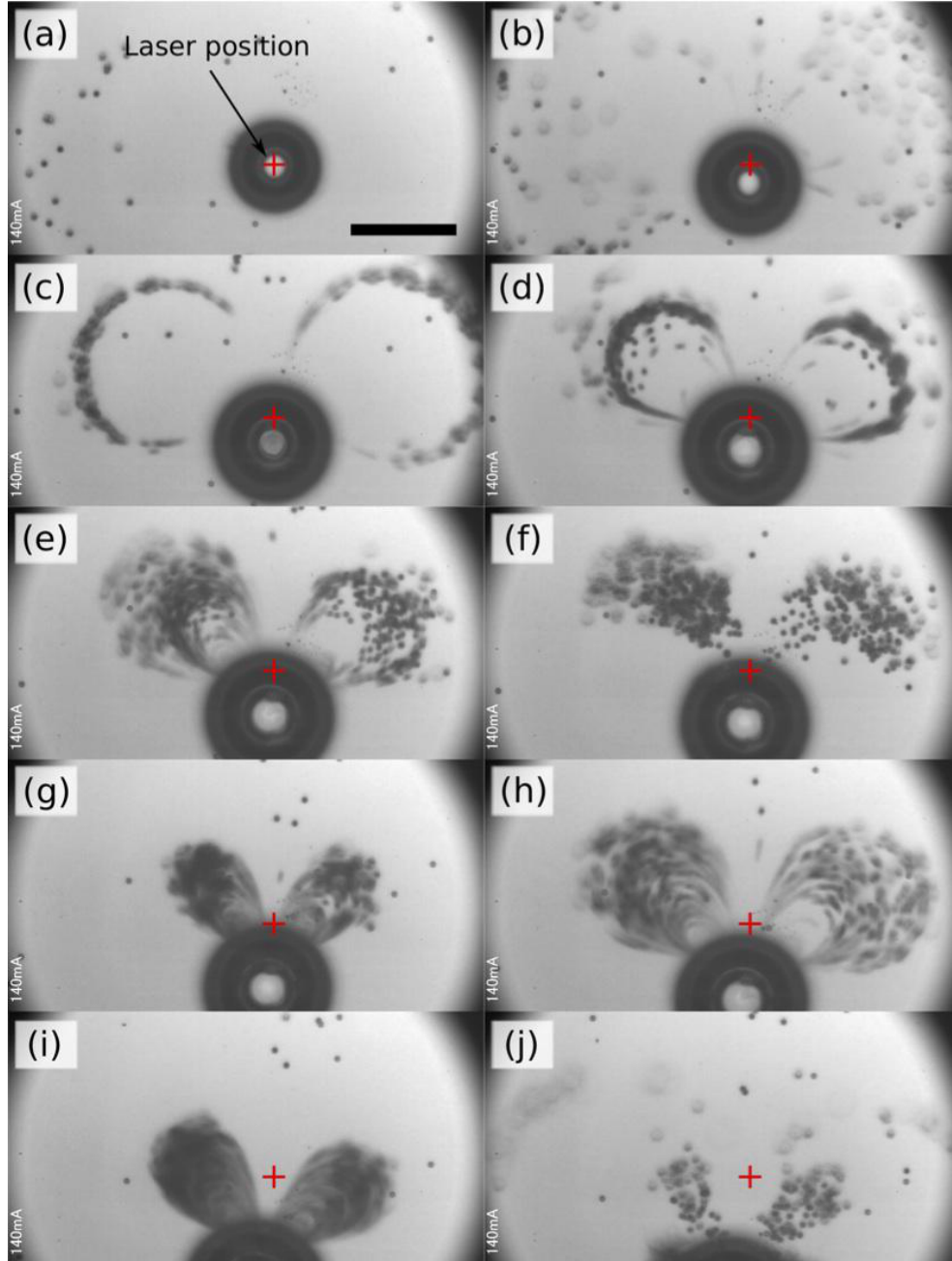


Figure 6.3: (a)–(j) Series of microscopic images showing dependence of the transformation of the flow around the micro bubble on the position of the laser spot. The red crosses show laser positions, the small black dots are polystyrene spheres, and the big black circles are the micro bubble, respectively. Scale bar: 50 μm .

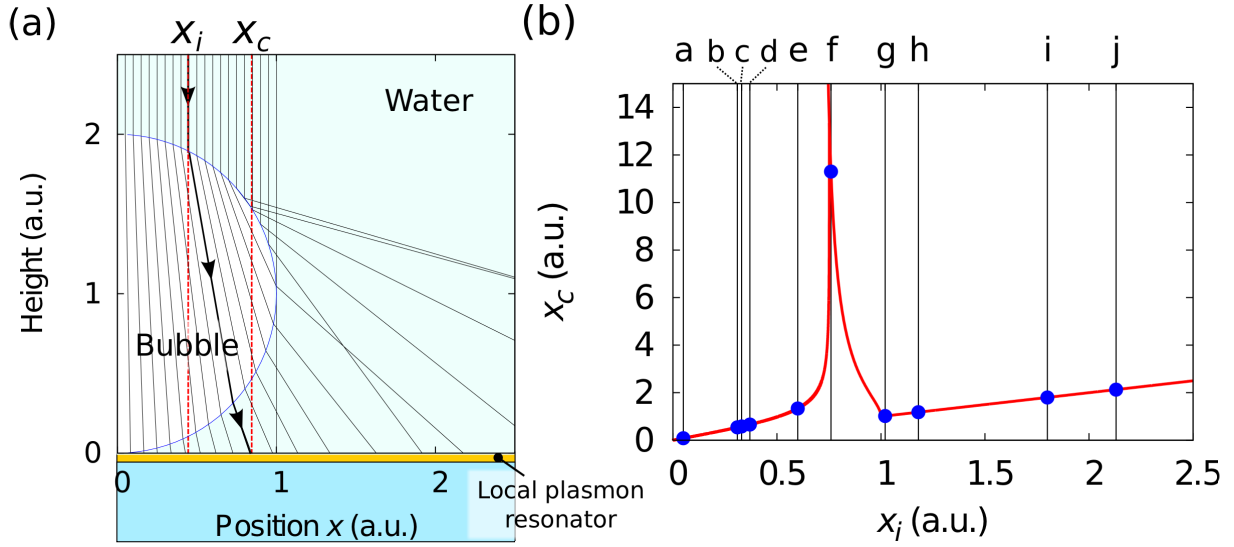


Figure 6.4: (a) Cross-sectional view of the cell with the optical paths (black lines) indicated. The scale is normalized to the bubble radius. (b) Red line represents the photothermal conversion position, x_c , as a function of the laser irradiated position, x_i . Letters over the figure correspond to Figs. 6.3(a)–6.3(j) whose relative positions of the bubble and the laser spot are shown as blue dots.

to the edge of the bubble (Fig. 6.3 (g)), the rapid flow developed again and the polystyrene spheres collected and concentrated near the bubble. As the distance of the laser spot from the bubble edge was increased, the shape of the rotation flow varied again (Figs. 6.3 (g)–(i)). Finally, when the distance of the laser spot from the bubble exceeded $\sim 28 \mu\text{m}$, the rapid flow stopped. These results suggest that by tuning the relative position of the laser spot and the bubble, we can develop a rapid flow with a wide variety of functions such as driving, mixing, ranging, and collecting the polystyrene spheres. For better understanding of the transformation of the flow, we focused our attention on light refraction and reflection at the bubble surface and evaluated the actual photothermal conversion position.

Figure 6.4 (a) corresponds to a cross sectional view of the sample cell whose scale is normalized by the bubble radius. The black lines in Fig. 6.4 (a) show ideal light paths going through a spherical vapor-water boundary. Although a ray of light splits into a number of rays after experiencing multiple refractions and/or reflections, we only consider the dominant light path for the photothermal heating of the bubble. Depending on the position of the laser irradiation, the position where the local plasmon resonator absorbs light varies significantly. Thus, we plot the photothermal conversion position, x_c , as a function of the laser irradiated position, x_i (Fig. 6.4 (b)). At around $x_i = 0.75$, the value of x_c has a distinct peak indicating

that the photothermal conversion position is far away from the bubble due to total reflection although the laser spot is placed on the bubble.

The evaluated photothermal conversion positions for the observed flows in Fig. 6.3 are represented in Fig. 6.4 (b). We normalized the laser position by the cross sectional bubble radius assuming that the contact angle of the sample cell wall with water is much lower than 90° . The laser position for Figs. 6.3 (a)–(j) are shown by vertical black lines in Fig. 6.4 (b). Among them, position (f) shows the farthest photothermal conversion position from the bubble, followed by the position (j). Therefore, absence of the rapid flow in Figs. 6.3 (f) and (j) is explained by their photothermal conversion position which is too distant to present a significant temperature gradient around the bubble. Positions (e) and (h) are similar in the photothermal conversion position ($x_c = 1.3$ for (e) and $x_c = 1.2$ for (h), respectively), whereby their rotation flows are equivalent in shape (Figs. 6.3 (e) and (h)). There is a tendency for the polystyrene spheres to concentrate near the bubble as the value of x_c becomes larger, except for the position (g). The high concentration of polystyrene spheres observed in Fig. 6.3 (g) may be due to the width of the actual laser spot, which results in a widespread value of x_c from 1 to ~ 2 because of its rather exponential change around $x_i = 1$ (Fig. 6.4 (b)). Although the photothermal conversion position is shown to be right underneath the bubble for the laser position (a), no significant flow was observed in Fig. 6.3 (a). This is because the water contact angle in the actual sample is not exactly zero and there is little water to drive at the center of the bubble. These results suggest that the flow development around the bubble can be characterized qualitatively by the position of the photothermal conversion. Further investigation of the transformation of the rotation flow requires numerical analysis that we plan to undertake in the future.

Here, we experimentally demonstrate the sorting of the polystyrene spheres with different diameters as one of the applications of the photothermally controlled Marangoni flow around a micro bubble. We prepared and filled the sample cell with a 1:1 mixture of the water suspension of polystyrene spheres with a diameter of $2\ \mu\text{m}$ (R0200, Thermo Scientific, diluted to 5% by water, particle number density: $\sim 1 \times 10^8\ \text{cm}^{-3}$) and of $0.75\ \mu\text{m}$ (42742, Alfa Aesar, diluted to 2% by water, particle number density: $\sim 2 \times 10^9\ \text{cm}^{-3}$). Figure 6.5 (a) shows the

uniformly dispersed polystyrene spheres with diameters of $2\ \mu\text{m}$ and $0.75\ \mu\text{m}$ before the laser irradiation. Following the experimental methods described above, we created a micro bubble and developed Marangoni flow around it using localized photothermal conversion of the local plasmon resonator. By optimizing the relative position of the laser spot and the micro bubble, the polystyrene spheres with different diameters are trapped in the rotation flows with different radius (Fig. 6.5 (b)). Figure 6.5 (c) clearly shows that the polystyrene spheres with diameters of $2\ \mu\text{m}$ and $0.75\ \mu\text{m}$ are segregate to different areas after the laser irradiation.

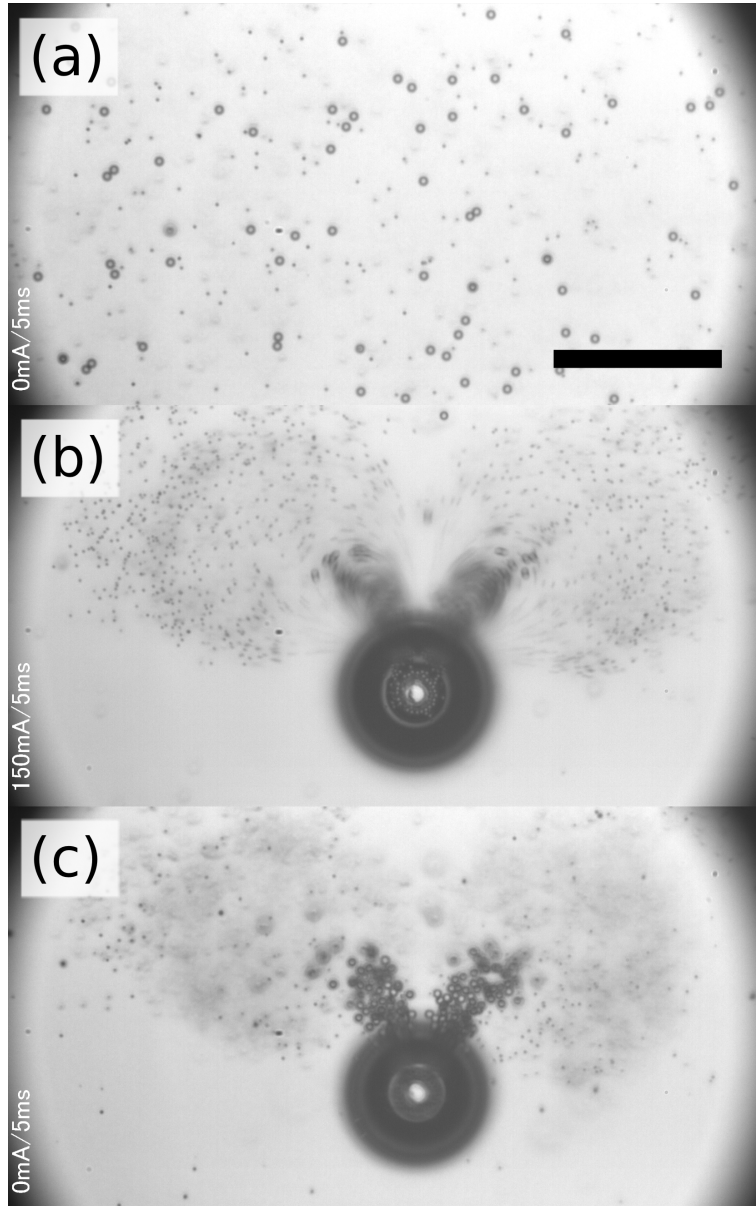


Figure 6.5: (a) Microscopic image of the sample cell before the laser irradiation, in which polystyrene spheres with diameters of $2\ \mu\text{m}$ and $0.75\ \mu\text{m}$ are well dispersed. (b) The controlled Marangoni flow around a photothermally created micro bubble. (c) Distribution of the polystyrene spheres after the sorting by Marangoni flow. Scale bar: $50\ \mu\text{m}$.

6.3.2 Evaluation of Flow Velocity

The images of the polystyrene spheres are elongated in the direction of the flow (Fig. 6.2(a)) because the spheres move more than several micrometers during the exposure time of the CCD camera. By dividing the stretch length of the particle image by the exposure time, we obtain the velocity of the particle, which indicates the flow velocity.

Figure 6.6 shows CCD images of the Marangoni flow around a microbubble taken with exposure times of (a) 5.0, (b) 1.0, and (c) 0.5 ms. The stretch length of the particle images increases with increasing exposure time, which proves that the elongation is due to the motion of the particles during the exposure time. In Figs. 6.6(b) and 6.6(c), the stretch length of the particle images near the bubble surface is obviously longer than that of the particle images at some distance from the bubble surface. In other words, the highest flow velocity is achieved around the bubble surface. This result is consistent with the fact that the microfluid is driven by the Marangoni force generated on the bubble surface. The stretch length of the particle indicated by a black arrow in Fig. 6.6(b) is more than $10\text{ }\mu\text{m}$. Therefore, given the exposure time of 1 ms, the velocity of the particle is estimated as more than 10 mm s^{-1} . This is the average velocity of the flow around the elongated particle image. The observed maximum flow velocity was $\sim 20\text{ mm s}^{-1}$, which is high enough for practical applications. To obtain more accurate and detailed flow velocity mapping around the microbubble, we need to introduce a particle image velocimetry method or particle tracking velocimetry method using a high-speed camera, which is our future work.

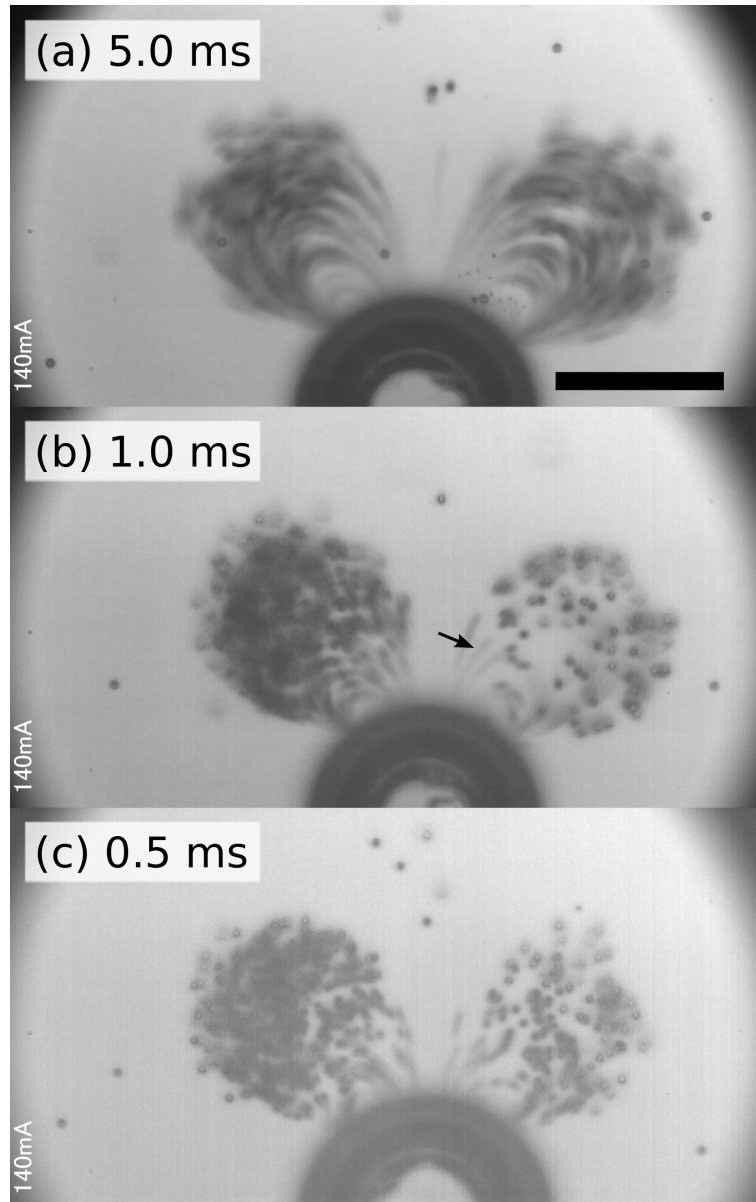


Figure 6.6: CCD images of Marangoni flow around a microbubble taken with exposure times of (a) 5.0, (b) 1.0, and (c) 0.5 ms. Scale bar: 50 μm .

6.4 Conclusion

In this chapter, we have demonstrated drastic transformation of the Marangoni flow around a micro bubble by using highly localized photothermal conversion of the local plasmon resonator. The highly localized photothermal conversion of the local plasmon resonator allowed us to create a micro bubble in the sample cell and to control the temperature gradient around the bubble at a micrometer scale. As a result, a rapid flow towards the bubble and two rotation flows develop around the bubble and the shape of the rotation flow was proved to be controllable by the relative position of the bubble and the photothermal conversion position. Using photothermally controlled Marangoni flow, we successfully demonstrated sorting of the PS spheres with diameters of $2\text{ }\mu\text{m}$ and $0.75\text{ }\mu\text{m}$ according to their size.

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Chapter 7

Concluding Remarks and Outlook

In this thesis, the photothermal properties of local plasmon resonators having Au nanoparticle (NP)/shape control layer/phase control layer/Ag mirror structures were investigated. Their optical absorption was characterized by the local plasmon resonance in the Au NPs, which is strongly assisted by interference. Because of the highly localized photothermal conversion in the Au NP layer and the controllability of the photothermal conversion efficiency by interference, the local plasmon resonators realize spatiotemporal control of the local temperature gradient, which is shown to be applicable for microfluidic control. These studies have proved their versatile functions, which include microheating, sound emission, and microfluidic manipulation, in addition to their excellent performance as surface-enhanced Raman spectroscopy sensors. It is noteworthy that all of these functions are available using exactly identical structures. Therefore, a simple system consisting of local plasmon resonators and a laser can be used as a versatile microfluidic platform providing manipulation, reaction, and sensing of molecules at arbitrary times and positions.

Publication List

Journal papers

This thesis is based on the following papers:

- [1] K. Namura, M. Suzuki, K. Nakajima, and K. Kimura, “Heat-generating property of a local plasmon resonator under illumination,” *Optics Letters* **36**(18), 3533–3535 (2011).
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Awards

[1] Best Student Presentation Award:

K. Namura, M. Suzuki, K. Nakajima, K. Kimura, “Spatiotemporal-photothermal and photoacoustic conversions with local plasmon resonators”, in SPIE Optics + Photonics 2011 (August 2011).

[2] 優秀ポスター賞:

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名村今日子 (July 2012).

[5] 第 37 回（2014 年秋季）応用物理学会講演奨励賞:

K. Namura, K. Nakajima, K. Kimura, M. Suzuki, “Microfluidic control by temporally modulated thermoplasmonics”, in 2014 年秋季 第 75 回応用物理学関係連合講演会 (September 2014).