Development of Pressure Sensitive Molecular Film as a Measurement Technique for High Knudsen Number Conditions

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Abstract.
To measure pressure distribution in high Knudsen number regimes, we have adopted a pressure sensitive paint (PSP) technique. Because a PSP works as a so-called "molecular sensor", it seems suitable for analyses of high Knudsen number flows, which require diagnostic tools in the molecular level. However, application of PSPs to micro-devices is very difficult because conventional PSPs are very thick compared to the dimension of micro-devices owing to the use of polymer binders. Moreover, they have not sufficient spatial resolution for pressure measurement of micro-flows because of the aggregation of luminescent molecules in polymer binders. In this study, we have adopted Langmuir-Blodgett (LB) technique to fabricate pressure sensitive molecular films (PSMFs) using Pd(II) Mesoporphyrin IX (PdMP) to resolve the problems of ordinary PSPs mentioned above, and have tested these PSMFs to evaluate the feasibility of the pressure measurement around micro-devices. The LB method is the technique to provide us with capability to construct ordered monolayer of molecules. A PSMF with nanometer order thickness and high spatial resolution is suitable for analyses of micro-flow. The fundamental properties of the PSMFs such as the pressure sensitivity and the surface roughness are examined, to evaluate the feasibility of the PSMF technique for pressure measurement around the micro-devices. It is clarified that the PSMF composed of PdMP (luminophore) and arachidic acid (buffer molecules) has enough pressure sensitivity in low pressure region with high Knudsen number, even if the amount of the luminescent molecules in the PSMF layer is much smaller than that in conventional PSPs. The results indicate the feasibility of PSMF technique to pressure measurement in high Knudsen number flows such as micro-flows.

Keywords: Flow Measuremnt, Rarefied gas Flow, High Knudsen Number Flow, PSP, LB Film
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INTRODUCTION

Experimental analyses of thermo-fluid phenomena with high Knudsen number, related to micro- and nano-technologies, need the molecular level measurement technique based on interaction of atoms or molecules with photons. However, the measurement techniques are behind in development compared with simulation techniques in the molecular level (e.g. DSMC). In the case of gas flows inside micro-systems, measurement of pressure on the surfaces has almost never been reported and development of its measurement technique has been eagerly anticipated. Of course, it is not realistic to apply pressure taps to micro-systems, because dimensions of typical pressure taps are comparable to those of micro-systems. Recently, pressure sensitive paint (PSP) has actively developed to measure two-dimensional pressure distributions of solid surfaces[1, 2, 3]. Because the PSP technique utilizes quenching of the luminescent molecules by oxygen molecules, it seems suitable for analyses of high Knudsen number flows, which require diagnostic tools in the molecular level. However, application of the PSP technique to a micro-system is very difficult, because the layer of a conventional PSP is too thick (larger than 5μm) owing to the use of polymer binder, and the aggregation of luminescent molecules cause low spatial resolution. In this study, we have adopted Langmuir-Blodgett (LB) method[4] to fabricate a pressure sensitive molecular film (PSMF) applicable to pressure measurement around micro-devices. Because the LB method can construct ordered molecular assemblies, a PSMF with nanometer order thickness and high spatial resolution seems suitable for analyses of micro-flows.

LUMINESCENCE PROPERTIES OF PSP

The pressure measurement technique using PSP is based on oxygen quenching of luminescence. When the PSP layer applied to the surface is irradiated by UV light, the luminescent molecules at the ground singlet state can be excited by absorption of photon energy to a higher singlet state. After the transition of the excited molecules from the singlet

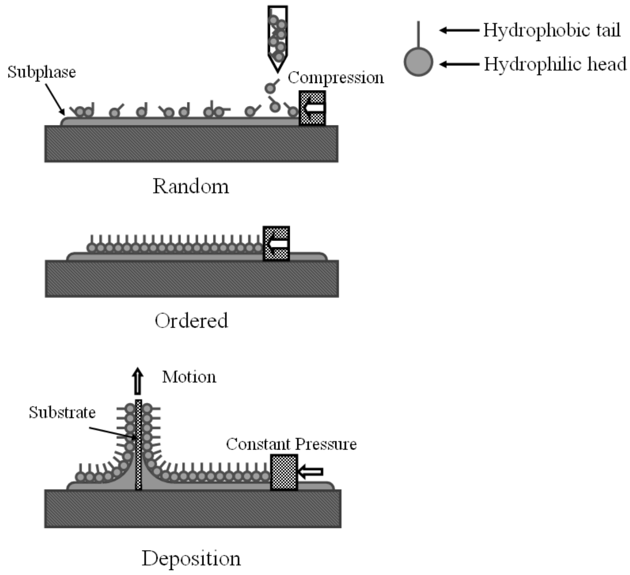


FIGURE 1. A schematic process of LB method

state to the lowest triplet state by an intersystem crossing, the molecules emit phosphorescence and transfer to the ground singlet state. Because the transition between the triplet state and the singlet state is spin forbidden, the lifetime of the phosphorescence is long. On the other hand, oxygen molecules with triplet ground state act as a quencher of the luminescence. As a result, the phosphorescence intensity decreases as an increase in partial pressure of oxygen. Pressure on the solid surface can be deduced from the relationship between pressure and the luminescence intensity called as Stern-Volmer relation[2, 3].

$$\frac{I_{ref}}{I} = A_0 + A_1 \frac{P}{P_{ref}} \tag{1}$$

where I is the luminescence intensity and P is the oxygen pressure. I_{ref} is the luminescence intensity at the known reference pressure P_{ref}. A_n are the constants called as Stern-Volmer coefficients determined by calibration tests. The luminescence intensity I of the ideal PSP depends inversely on P following to Eq.(1), but the actual PSPs have nonlinear dependence of I^{-1} on P. Therefore, the following equation considering the nonlinearity should be employed:

$$\frac{I_{ref}}{I} = \sum_{n=0}^{N} A_n \left(\frac{P}{P_{ref}} \right)^n \tag{2}$$

In practice, a second-order polynomial ($N = 2$) is commonly used.

EXPERIMENTAL METHODS

Formation of pressure sensitive molecular film

In this study, we have adopted Langmuir-Blodgett (LB) method[4] to fabricate a pressure sensitive molecular film (PSMF) with ordered molecular structure applicable to pressure measurement around micro-devices. The LB method provides us with capability to construct ordered molecular assemblies. LB films are fabricated according to the following procedure. At first, a drop of a dilute solution of amphiphilic molecules in a volatile solvent is spread on the interface between air and subphase. After the solvent is evaporated, a monolayer of the molecules remains on the interface. The monolayer is transferred to a substrate with compressing the monolayer so as to control the order of the molecules (see Fig. 1). A PSMF with nanometer order thickness and high spatial resolution seems suitable for analyses of micro-flows. Palladium(II) Octaethylporphine (PdOEP) has been adopted as luminescent molecule of PSMF. A conventional PSP composed of PdOEP has high pressure sensitivity in low pressure region[5]. We have

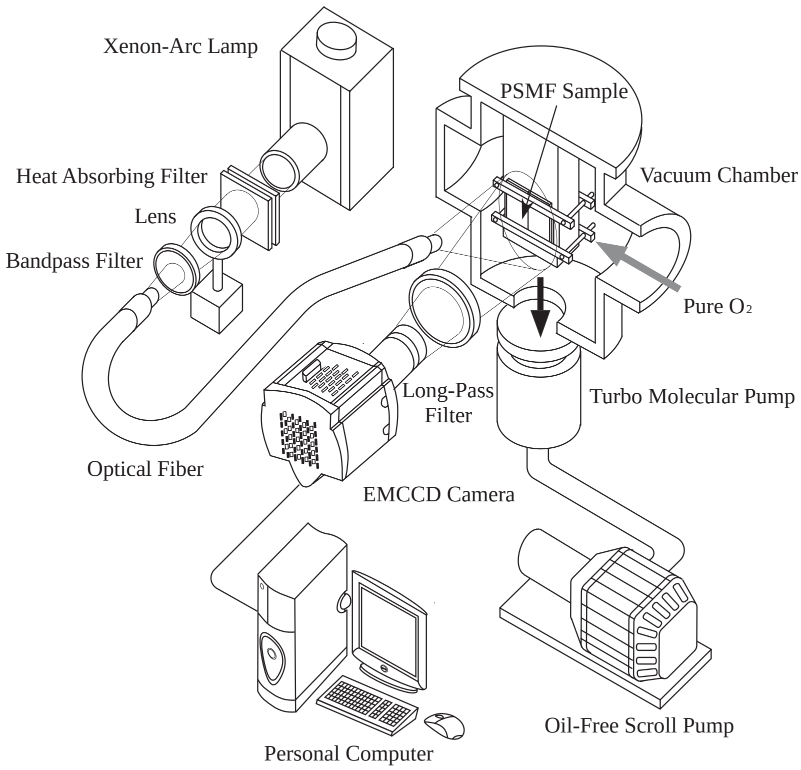


FIGURE 2. Experimental Apparatus

also applied Pd(II) Mesoporphyrin IX (PdMP), one of the amphiphilic palladium porphyrin, as a luminophore of the PSMF, because only amphiphiles can form stable LB films. We have prepared three types of samples with 2, 6, and 20 monolayers of PSMFs deposited on a glass plate.

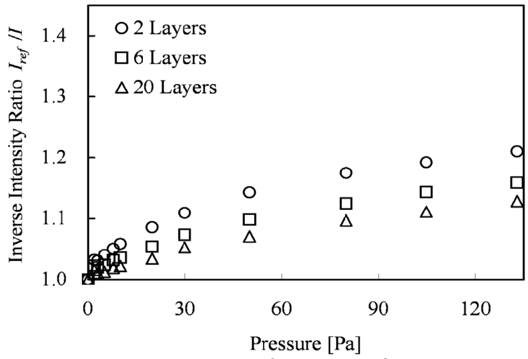
Experimental apparatus

Figure 2 shows the experimental apparatus composed for this study. The PSMF samples are set inside a vacuum chamber evacuated by a scroll pump (Ulvac, DVS-631) and a turbo molecular pump (Ulvac, UTM-300). Oxygen gas is supplied into the chamber to control the oxygen pressure in the chamber, and the pressure is monitored by a capacitance manometer (Ulvac, CCMT-10A) and an ionization vacuum gauge (Ulvac, GI-M2). A xenon-arc lamp (Ushio, UXL-500SX) with a band-pass filter (400$\pm$20 nm) is used as an excitation light source irradiating the sample via an optical fiber. The luminescence is filtered by a long-pass filter (540 nm) to eliminate the light from the xenon lamp, and is detected by an Electron Multiplying CCD (EMCCD) camera (Andor Technology, DV887AC-UV). The image of the luminescence is processed by a personal computer to obtain the pressure map on the sample.

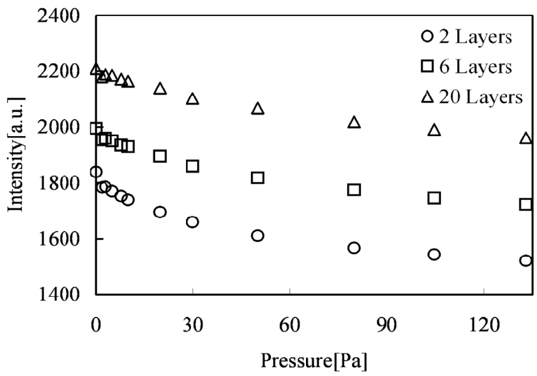
RESULTS AND DISCUSSIONS

Pressure sensitivity of PSMF composed of PdOEP

In this study, we have fabricated PSMF composed of PdOEP and have tested pressure sensitivity of this PSMF in the pressure condition below 1.3×10^2Pa. Figure 3 shows the Stern-Volmer plots and the luminescence intensity for PSMFs of 2-layer, 6-layer and 20-layer. The horizontal axis of Stern-Volmer plots is the pressure P, the vertical axis is the inverse luminescent intensity ratio I_{ref}/I, where the I_{ref} is the luminescence intensity at the reference pressure



(a) Stern-Volmer plots for PSMF of PdOEP



(b) Luminescent intensity of PSMF of PdOEP

FIGURE 3. Stern-Volmer plots (a) and Luminescent intensity (b) for PSMF of PdOEP below 1.3×10^2Pa at 293K, where I_{ref} is the luminescent intensity at P_{ref} $(= 1.0 \times 10^{-2}\text{Pa})$

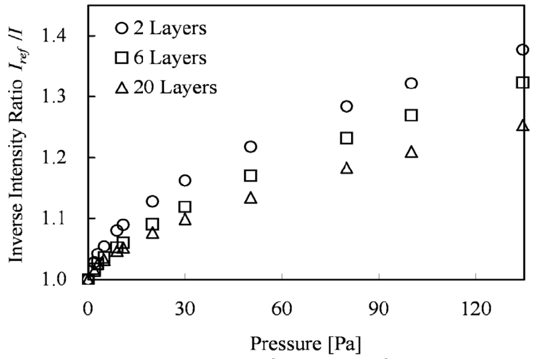
$P_{ref} = 1.0 \times 10^{-2}$Pa. It was found that pressure sensitivity of PSMF composed of PdOEP was not high enough to measure low pressure flows and micro-flows on the analogy of high Knudsen number flows.

Pressure sensitivity of PSMF composed of PdMP

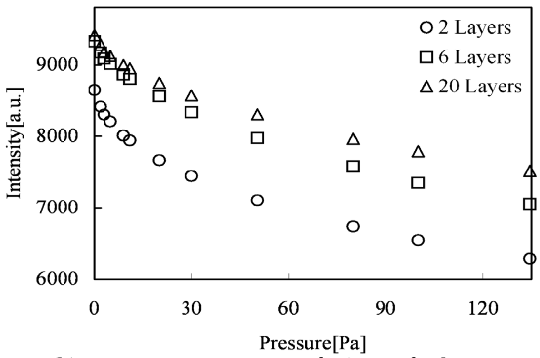
In this section, we have applied PdMP, one of the amphiphilic palladium porphyrins, as a luminophore of the PSMF, because amphiphiles can form stable LB films.

Figure 4(a) show the Stern-Volmer plots for PSMFs of 2-layer, 6-layer and 20-layer in the pressure condition below 1.3×10^2Pa, and figure 4(b) shows the luminescence intensity for PSMF of 2-layer, 6-layer and 20-layer. The horizontal axis of each Stern-Volmer plot is the pressure P, the vertical axis is the inverse luminescent intensity ratio I_{ref}/I, where the I_{ref} is the luminescence intensity at the reference pressure $P_{ref} = 1.0 \times 10^{-2}$Pa. It is shown that the PSMF of PdMP has sufficient pressure sensitivity in the low pressure region with high Knudsen number, even if the amount of the luminescent molecules in PSMF layer, whose thickness is in the order of nanometer, is much smaller than that in conventional PSPs, whose thickness is in the order of micron. It is found that the presssure sensitivity of PSMF composed of PdMP is higher than that of PSMF composed of PdOEP (see Fig.3(a)).

The sensitivity of the 2-layer PSMF is higher than that of the 6-layer and the 20-layer PSMFs. It is because the change of luminescence intensity is almost equal regardless of the number of layers (see Fig.3(b) and Fig.4(b)). The fact indicates that the oxygen molecule only interacts with the outermost layer, that is, oxygen quenching occurs at the outermost layer only. For the further improvement of pressure sensitivity, it is important to improve the oxygen permeability of the PSMFs.



(a) Stern-Volmer plots for PSMF of PdMP



(b) Luminescent intensity of PSMF of PdMP

FIGURE 4. Stern-Volmer plots (a) and Luminescent intensity (b) for PSMF of PdMP below 1.3×10^2Pa at 293K, where I_{ref} is the luminescent intensity at P_{ref} $(= 1.0 \times 10^{-2}$Pa)

Application of PSMF to pressure measurement

In this study, we measured the pressure distribution of the solid surface interacting with supersonic free-jet, as an application of our PSMF to low-density gas flows. The experimental setup is as follows. The converging nozzle is attached at the supply port of oxygen gas. The nozzle diameter is 0.53mm, the impinging angle is 60 deg, and the distance between nozzle end to the solid surface is 2mm. The stagnation pressure and the back pressure are set at 1.3×10^3Pa and 1.3Pa, respectively.

Figure 5 shows the pressure distribution on the surface detected by PSMF composed of PdMP. The image of the pressure distribution can be obtained qualitatively, although it contains noises because the amount of luminescent molecules of PSMF is smaller than that of conventional PSP. This result indicates the usefulness of our PSMF for measurement of low-density gas flows in spite of small luminescent molecules and small number of collision between gas molecules and solid surface.

SUMMARY

We have examined pressure sensitivity of pressure sensitive molecular films (PSMFs) using Palladium(II) Octaethylporphine (PdOEP) and Pd(II) Mesoporphyrin IX (PdMP) as luminophores in low pressure conditions, to clarify the feasibility of PSMF for measurement of surface pressure in high Knudsen number flows such as micro-flows. The following concluding remarks are obtained:

1. It is shown that the PSMF fabricated in this study has sufficient sensitivity in the low pressure region with high

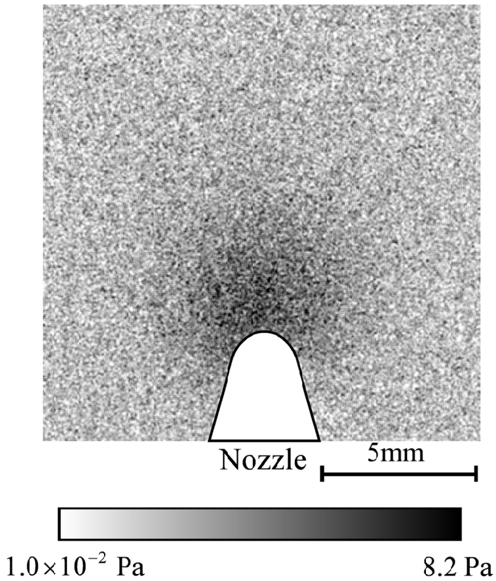


FIGURE 5. Pressure distribution on solid surface interacting with an impinging supersonic free-jet

Knudsen number, even if the amount of the luminescent molecules in PSMF is smaller than that in conventional PSP.

2. It is clarified that the PSMF composed of Pd(II) Mesoporphyrin IX (PdMP) has higher sensitivity than that of Pd(II) Octaethylporphine (PdOEP).
3. The pressure sensitivity of the 2-layer PSMF is higher than that of the 6-layer and the 20-layer PSMFs, because oxygen quenching occurs at the outermost layer only.
4. The pressure distribution on the solid surface interacting with supersonic free-jet can be measured with PSMF composed of PdMP. It is showed that the usefulness of our PSMF for measurement of low-density gas flows.

As a result, the PSMF composed of PdMP is feasible to measure the pressure in high Knudsen number flows such as micro-flows.

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