Molecular number flux detection using oxygen sensitive luminophore

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Experimental analyses of thermofluid phenomena with a high Knudsen number, related to low-density gas flows or nanotechnologies, need the measurement techniques based on atoms or molecules, such as emission and absorption of photons. Because the principle of the pressure sensitive paint (PSP) technique is based on oxygen quenching of luminescence, the technique has the capability to be applied to high Knudsen number flows such as microflows and low-density gas flows. In this study, to inspect the feasibility of PSP for measurement of pressure on a solid surface in high Knudsen number flows, fundamental properties of three types of PSP [palladium tetrakis (pentafluorophenyl) porphyrin, palladium octaethylporphyrin (PdOEP), and platinum tetrakis (pentafluorophenyl) porphyrin bound by poly[1–(trimethylsilyl)-1–propyne] (poly(TMSP))] are examined especially in the range of pressure below 130 Pa (about 1 Torr). As an application of PSP to high Knudsen number flows, we measure the pressure distribution on a jet-impinging solid surface using PdOEP/poly(TMSP) with very high sensitivity. Moreover, the "pressure" distribution obtained by the PSP is compared with the distribution of the molecular number flux onto the solid surface to investigate the feasibility of number flux measurement by PSP. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1921927]

I. INTRODUCTION

Experimental analyses of thermofluid phenomena with a high Knudsen number, related to low-density gas flows or nanotechnologies, need the measurement techniques based on atoms or molecules, such as emission and absorption of photons. However, such measurement techniques are behind in development compared with the molecular simulation techniques. For example, in the case of gas flows inside microsystems and nanosystems, 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 microsystems, because dimensions of typical pressure taps are comparable to those of the microsystems.

Recently the pressure sensitive paint (PSP) has been actively developed to measure two-dimensional pressure distributions on solid surfaces.[1–4] Generally, the pressure range of PSP has been limited above 1 Torr (133 Pa), and there have been no applications to the lower pressure range other than those by the authors,[3,4] because the pressure sensitivity of the PSP technique seemed to be not so high in the range. Because the PSP technique utilizes quenching of the luminescence by oxygen molecules; however, it seems suitable for analyses of high Knudsen number flows, which require diagnostic tools in the molecular level.

The sensitivity of PSPs depends mainly on the quenching probability of the luminophore as well as the oxygen permeability of the binder. In the previous study,[3,4] we have clarified that a glassy polymer poly[1–(trimethylsilyl)-1–propyne] [poly(TMSP)] with extremely high oxygen permeability is a suitable binder of PSP for low-pressure condi-

tions, because poly(TMSP)-based PSP shows very high pressure sensitivity and no hysteresis property. To increase the pressure sensitivity further, luminophores with high quenching probability should be selected. In this study, we have tested three kinds of porphyrins to select suitable luminophores. One of the luminophores is platinum tetrakis (pentafluorophenyl) porphyrin (PtTFPP), which has been commonly used as a luminophore of PSP, and the others are palladium porphyrins, palladium octaethylporphyrin (PdOEP) and palladium tetrakis (pentafluorophenyl) porphyrin (PdTFPP). We have examined their fundamental properties such as pressure sensitivity and temperature dependence of luminescence intensity in the range of pressure below 1 Torr. Moreover, pressure distributions on a small solid surface interacting with low-density supersonic free jets are measured by the PSP, showing the applicability of PSP to high Knudsen number conditions.

However, since PSP is based on the interaction of oxygen molecules with luminescent molecules, we consider that the luminescence intensity of PSP must relate to the molecular number flux onto the solid surface, rather than the surface pressure. If so, the oxygen sensitive luminophores will become a useful tool to measure the molecular number flux in high Knudsen number regime, in which the flow should not be considered as a continuum flow but as a flow of molecules.

II. LUMINESCENCE PROPERTIES OF PSP

The pressure measurement technique using PSP is based on oxygen quenching of luminescent molecules.[1,2] The PSP is composed of luminescent molecules and a binder material to fix the luminescent molecules to a solid surface. When the PSP on the surface is irradiated by UV or visible light, the

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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 state to the lowest triplet state by an intersystem crossing, the molecules emit phosphorescence and get transferred 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 relatively long. On the other hand, oxygen molecules, whose ground state is triplet, act as quenchers of the luminescence. As a result, the phosphorescence intensity decreases the partial pressure of oxygen increases. Pressure on the solid surface can be deduced from the relationship between the pressure and the luminescence intensity (Stern–Volmer plot).[1]

Luminescence quantum yield Φ of PSP is given by

$$\Phi = \frac{I}{I_a} = \frac{k_L}{k_L + k_D + K_Q[O_2]} = k_L \tau, \tag{1}$$

where I is the luminescence intensity and I_a is the absorption intensity. k_L, k_D, and K_Q are the rate constants for luminescence, radiationless deactivation, and oxygen quenching, respectively. $[O_2]$ is the concentration of oxygen molecules and τ the lifetime of an excited luminescent molecule.

From Eq. (1), the ratio of the luminescence intensity I to that in the absence of oxygen molecules, I_0, is given by

$$\frac{I_0}{I} = \frac{k_L + k_D + K_Q[O_2]}{k_L + k_D} = 1 + \frac{K_Q[O_2]}{k_L + k_D} = 1 + K_Q \tau_0 [O_2], \tag{2}$$

where τ_0 is the lifetime of an excited molecule in the absence of oxygen molecules. If we assume that the concentration $[O_2]$, the partial pressure of oxygen gas P_{O_2}; and the total pressure P follow the relation $[O_2] \propto P_{O_2} \propto P$, then Eq. (2) can be reduced to the form

$$\frac{I_0}{I} = 1 + KP, \tag{3}$$

where K is a constant. In a practical application of PSP, it is usually difficult to measure I_0 to calibrate the PSP. If the luminescence intensity of the PSP, I_{ref}, is obtained at the known reference pressure P_{ref}, Eq. (3) is modified as follows:

$$\frac{I_{ref}}{I} = A_0 + A_1 \frac{P}{P_{ref}}. \tag{4}$$

A_n are the constants called as Stern–Volmer coefficients determined by calibration tests. In principle, I_{ref}/I depends linearly on P/P_{ref} according to Eq. (4), but the actual PSPs have nonlinear dependence of I_{ref}/I on P/P_{ref}. Therefore, the following equation considering the nonlinearity should be employed:

$$\frac{I_{ref}}{I} = \sum_{n=0}^{N} A_n \left(\frac{P}{P_{ref}} \right)^n. \tag{5}$$

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

It should be noted that the coefficients A_n have the dependence on the temperature of the solid surface, because

both the quenching probability of luminescent molecules and the oxygen permeability of binder depend on temperature. Therefore, the effect of the temperature must be eliminated for the precise measurement of pressure.

III. EXPERIMENTAL SETUP

Figure 1 shows the experimental apparatus composed for this study. The PSPs are painted on aluminum plates (50 $\times$ 25 mm^2) by an airbrush and then the plates are set inside a vacuum chamber evacuated by a scroll pump (ULVAC DVS-631) and a turbomolecular pump (ULVAC UTM-300). Pure oxygen gas (purity: more than 99.99%) is supplied into the chamber through a pressure control valve, and the pressure is monitored by a capacitance manometer and an ionization vacuum gauge. The temperature of the PSP sample is controlled by a Peltier thermocontroller and is monitored by a thermocouple. A xenon arc lamp with a bandpass filter is used as an excitation light source, and the light is transmitted via an optical fiber. The wavelength range of the bandpass filter is 400$\pm$20 nm, which overlaps the absorption band of the luminophores. The luminescence is filtered by a short-cut filter (600 nm) to eliminate the incident light from the xenon arc lamp and is detected by a charge-coupled device (CCD) camera (Hamamatsu C4742-95, 1280$\times$1024 pixels, 12 bit) with an image intensifier. In this study, we set the integration time of the camera as 120 ms per frame, and five frames were integrated to obtain each datum of the image. The image of the luminescence is stored in a personal computer.

To measure a pressure distribution on a solid surface interacting with a supersonic free jet, a converging nozzle can be installed at the gas supply port inside the chamber. The jet expands through the nozzle and impinges on the PSP sample with the angle of attack of 60°. The diameter of the nozzle exit, D, is 0.5 mm, and the distance along the centerline of the jet from the nozzle exit to the surface is 2 mm. The arrangement of the nozzle and the sample surface is also depicted in Fig. 1.

In this study, we have tested three kinds of porphyrins to select the suitable luminophore. One of the luminophores is PtTFPP, which has been commonly used as a luminophore of PSP and was tested in the previous study,[3,4] and the others are palladium porphyrins, PdOEP and PdTFPP, which are reported to have higher oxygen sensitivity than platinum porphyrins,[5] especially in the range of low pressure. All of the luminophores listed above are bound by poly(TMSP), a glassy polymer with very high oxygen permeability.[4]

IV. RESULTS AND DISCUSSIONS

A. Properties of pressure sensitive paints in low pressure

Figure 2 shows the Stern–Volmer plot of PSPs using poly(TMSP) as a binder against oxygen pressure. The reference pressure P_{ref} was 1.0×10^{-2} Pa for (a) and 1.3×10^2 Pa for (b), and the temperature T was kept at 300 K for the both cases. As easily seen in Fig. 2(a), both PdOEP and PdTFPP have extremely high pressure sensitivity in the low-pressure condition below 130 Pa (about 1 Torr). How-
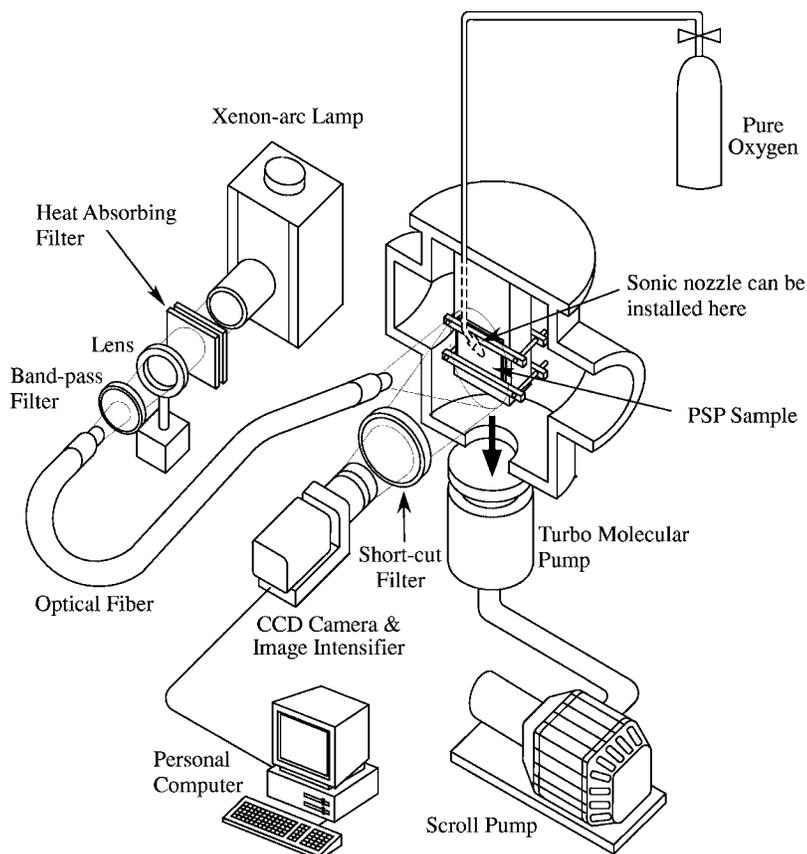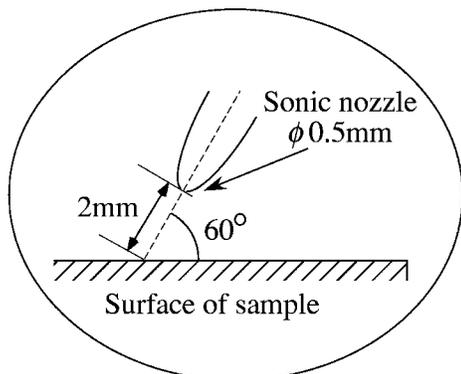
FIG. 1. Experimental apparatus.

ever, the pressure sensitivity of PdOEP and PdTFPP in a relatively high pressure above 130 Pa decreases gradually as shown in Fig. 2(b), showing the strong nonlinearity of the Stern–Volmer plots. Because the luminescence of both PdOEP and PdTFPP is highly quenched and saturated at the pressure above 130 Pa, the dependence of the luminescence intensity on the oxygen pressure disappears. As a result, PdOEP and PdTFPP bound by poly(TMSP) would be very powerful measurement tools in the low-pressure condition below 130 Pa, although they cannot be applied in the higher pressure range. The result implies that the two PSPs can be applied to microsystems whose Knudsen number is also high.

B. Error in pressure measurement caused by surface temperature

As mentioned in Sec. II, the luminescence intensity depends not only on the oxygen pressure, but also on the surface temperature, because the Stern–Volmer coefficients A_n are functions of the surface temperature T. Therefore, the temperature change on the surface may cause an error in the pressure measurement.

In this study, we have investigated the dependence of the luminescence intensity of the PSP on the surface temperature. Figure 3 shows the dependence of the luminescence intensity of PdOEP on the surface temperature at the oxygen pressure of 1.0×10^{-2} Pa, 1.3 Pa, and 130 Pa. The vertical
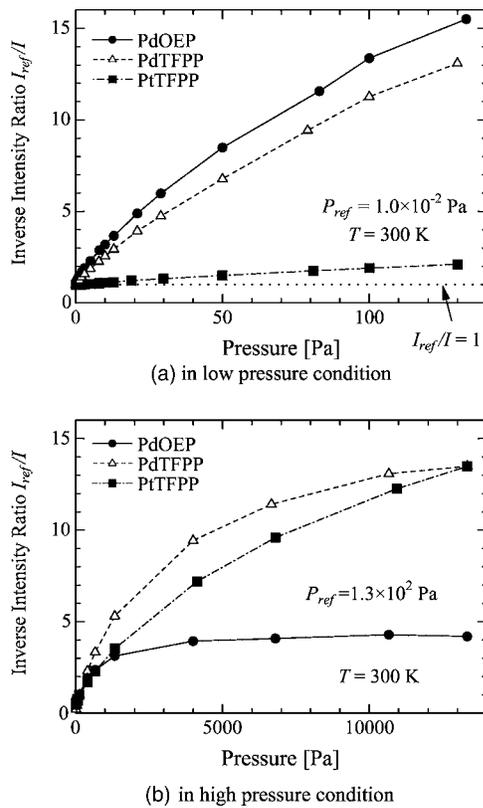
FIG. 2. Stern–Volmer plots of PSPs.

axis indicates the ratio of the luminescence intensity, I_{275}/I (I_{275} is the intensity at 275 K in each pressure condition). As clearly seen in the figure, PdOEP has distinct dependence of the luminescence intensity on the temperature. In Fig. 3, only the results of PdOEP are shown, but the other PSPs, PdTFPP, and PtTFPP have the similar dependence on the temperature. Because the dependence of the luminescence intensity on the temperature is comparable to that on the oxygen pressure, the dependence should be considered when the pressure is deduced from the luminescence intensity, especially for applications in low-pressure conditions.

C. Application of PSP in high Knudsen number regime: Measurement of pressure distribution on a solid surface interacting with a low-density jet

As an application of PSP in a high Knudsen number condition, PdOEP bound by poly(TMSP), having very high sensitivity in low-pressure conditions, was applied to mea-
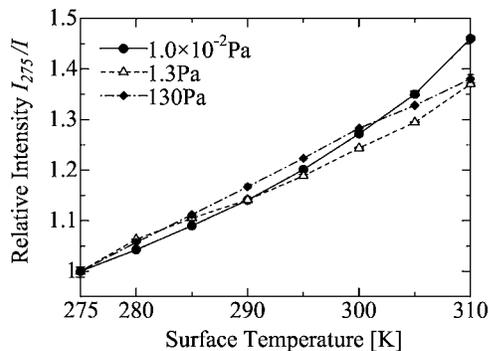

FIG. 3. Temperature dependence of luminescence intensity of PdOEP.
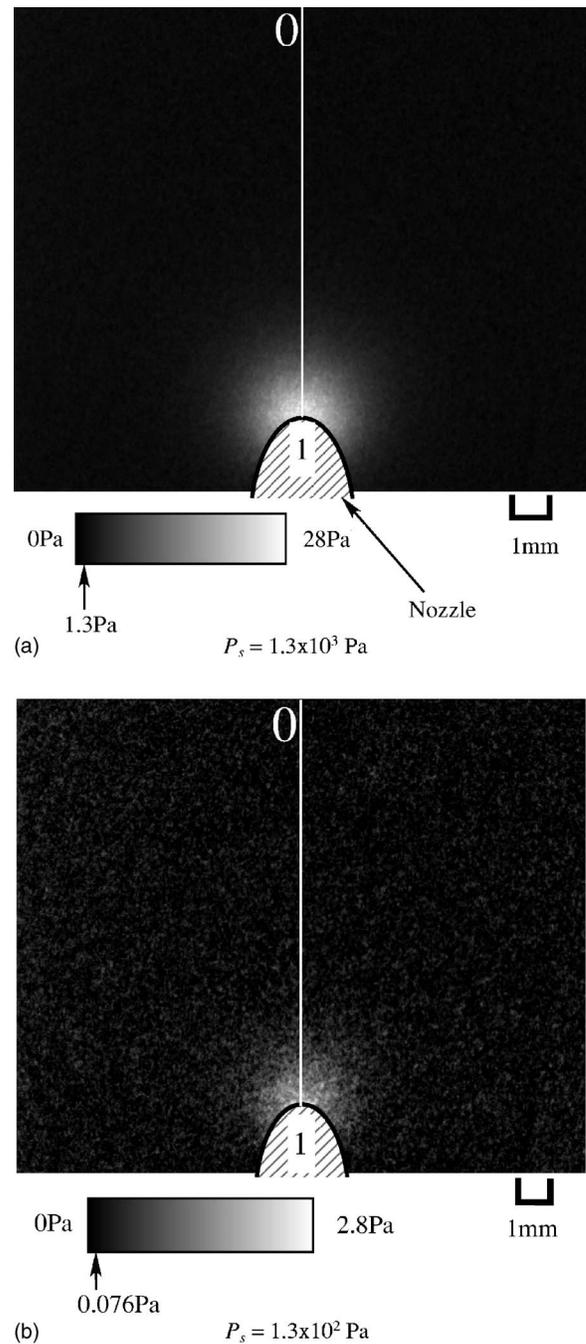

FIG. 4. Two-dimensional pressure distribution of jet-impinging surface measured by the PSP.

sure pressure distributions on an aluminum plate interacting with a supersonic free jet. The arrangement of the jet and the plate is depicted in Fig. 1. Pure oxygen was used as a test gas for the experiments, and the source pressure P_s was set at 1300 Pa and 130 Pa. The resulting background pressure P_b was 1.3 Pa and 7.6×10^{-2} Pa, respectively. For $P_s = 1300$ Pa, the mean-free path at the impingement point on the centerline of the jet is estimated as 1.12 mm, assuming an isentropic flow, and the Knudsen number is obtained as 2.24. For $P_s = 130$ Pa, the Knudsen number is estimated as 22.4 in the same manner by using the nozzle diameter D of 0.5 mm as the characteristic dimension.

TABLE I. Stern–Volmer coefficients of PdOEP/poly(TMSP).

	(a) $P_s=1.3\times10^3$ Pa	(b) $P_s=1.3\times10^2$ Pa
P_{ref}(Pa)	1.3	7.6×10^{-2}
A_0	8.7×10^{-1}	1.0
A_1	1.3×10^{-1}	8.5×10^{-3}
A_2	-9.4×10^{-4}	-8.0×10^{-6}

As mentioned above, since the temperature change of the surface affects the pressure measurement by PSPs, the plate was kept at 300 K by using a Peltier thermocontroller. In addition, the temperature distribution on the surface interacting with the jets was measured by using a temperature sensitive paint, europium (III) thenoyltrifluoroacetonate [Eu(TTA)$_3$] bound by poly(methyl methacrylate) (PMMA), in the same condition. As a result, the width of the temperature distribution was less than ±2 K, corresponding to the error in pressure measurement of ±0.17 Pa.

Figures 4(a) and 4(b) show the pressure distributions measured by the PSP for P_s=1300 Pa and 130 Pa, respectively. In the pictures, 1 mm over the surface corresponds to 57 pixels of the images obtained by the CCD camera, indicating the spatial resolution of the images is 18 μm. The images do not indicate the luminescence intensity distributions themselves, but the calibrated two-dimensional pressure distribution maps; white color corresponds to high-pressure regions and black color to low-pressure regions. The Stern–Volmer coefficients in Eq. (5) used for the calibration are listed in Table I along with the reference pressure P_{ref} for each case. Figure 5 shows the pressure distribution along the projection of the centerline of the impinging jet for P_s=1300 Pa and 130 Pa. The horizontal axis refers to the position x on the projection line indicated in Fig. 4 (from the point "0" to "1") normalized by the nozzle diameter D. The broken line in the graph corresponds to the background pressure P_b.

For P_s=1300 Pa, a clear image of the pressure distribution was obtained [Fig. 4(a)]. Moreover, the pressure far from the nozzle exit approaches the background pressure with an accuracy of ±0.3 Pa, as plotted in Fig. 5(a). This fact indicates the feasibility of pressure measurement by the PSP at low-pressure conditions.

At the lower pressure condition of P_s=130 Pa, the image of the pressure distribution could be obtained, but there exists a significant noise in the image. The measured pressure distribution along the centerline shown in Fig. 5(b) fluctuates largely. Since the pressure range is very small (0–2.8 Pa), the signal-to-noise ratio becomes relatively low. The uncertainty in the measurement can be reduced by using a CCD camera with high intensity resolution.

In this study, the spatial resolution of about 18 μm has been achieved. However, the actual spatial resolution might be worse, because of the nonuniformity of the PSP layer, that is, the nonuniformity of the thickness of the layer, the distribution of the luminescent molecules in the layer, and the condensation or crystallization of luminescent molecules in
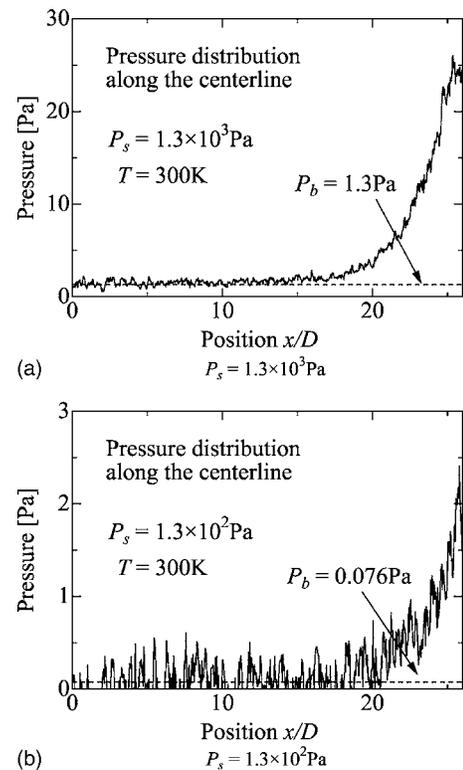

FIG. 5. Pressure distribution along the centerline measured by the PSP.

the polymer binder. Figure 6 shows a luminescence image of the sample of PtTFPP in poly(TMSP) obtained by using a fluorescence microscope (OLYMPUS BX61) at the atmospheric pressure. In the figure, crystallized luminescent molecules are observed, and the size of the crystals is of the order of 10–20 μm, which is comparable to the spatial resolution based on the instruments as mentioned above. Therefore, it is impossible to improve the spatial resolution by using a higher-resolution camera or other optical instruments. To improve the spatial resolution, new techniques to produce uniform films (e.g., Langmuir-Blodgett films) should be applied to the formation of PSP layers.

D. Measurement of number flux by PSP

As an application of PSP in high Knudsen number regime, we have mentioned the measurement of pressure dis-
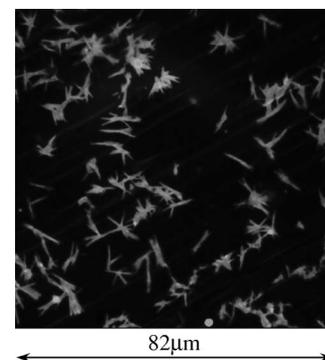

FIG. 6. Luminescence of PtTFPP in poly(TMSP).

tributions on solid surfaces interacting with rarefied gas flows. However, if the Knudsen number of a flow is larger than 0.1, the flow should not be considered as a continuum flow but as a flow of atoms and molecules. In this case, atomic or molecular number flux becomes important to analyze the interaction between the flow and solid surfaces.

Since PSP is based on the interaction of oxygen molecules with luminescent molecules, we consider that the luminescence intensity of PSP does not correspond to the surface pressure rigorously, but must relate to the molecular number flux onto the solid surface. Pressure is defined as a force exerted on a unit area, i.e., change in momentum of molecules colliding with the surface per unit area and unit time. On the other hand, number flux is defined as the number of molecules striking the surface per unit area and unit time. Because the PSP technique utilizes penetration of oxygen molecules into PSP layer and quenching of luminescent molecules by oxygen, it is plausible to consider that the luminescence intensity of PSP depends on the molecular number flux.

For a static gas, the molecular flux F_0 is given as $F_0 = n\bar{c}/4$,[6] where n is the molecular number density and $\bar{c}$ is the mean molecular speed. If a perfect gas is assumed, the relation between the pressure p_0 and F_0 is derived by using the equation of state $p_0 = nkT$ as

$$p_0 = \left(\frac{4kT}{\bar{c}}\right) \quad F_0 = \sqrt{2\pi mkT}F_0, \tag{6}$$

where k is Boltzmann's coefficient, T is the temperature, and m is the mass of a molecule. In this case, p_0 is proportional to F_0, and the pressure can be measured by the number flux deduced from the luminescence intensity of PSP. On the other hand, if a gas flow impinges perpendicular to a surface with the velocity v, the flux F turns out to be

$$F = n\sqrt{\frac{m}{2\pi kT}}\left\{\frac{kT}{m}\exp\left[-\frac{mv^2}{2kT}\right]\right.$$
$$\left. - \frac{v}{2}\sqrt{\frac{2\pi kT}{m}}\left[1 - \mathrm{erf}\left(v\sqrt{\frac{m}{2kT}}\right)\right]\right\}. \tag{7}$$

In this case, the static pressure p depends not only on F but also on v. Of course, the pressure on the solid surface is not equal to the static pressure but to the total pressure of the gas and it is proportional to the number flux, because the macroscopic velocity v is brought to zero in the vicinity of the solid surface. However, in high Knudsen number regime related to rarefied gas flows and microflows/nanoflows, the number flux becomes more important than the pressure, and the measurement technique of molecular number flux is needed for experimental analyses. The PSP technique would become a powerful tool to measure molecular number flux in high Knudsen number regime.

V. SUMMARY

We have examined the fundamental properties of PSPs using poly(TMSP) as a binder in low-pressure conditions to clarify the feasibility of PSP for measurement of surface pressure in high Knudsen number flows. The following concluding remarks are obtained.

(1) In the low-pressure conditions below 130 Pa, PdOEP and PdTFPP bound by poly(TMSP) show very high pressure sensitivity. Although this pressure sensitivity decreases rapidly at the pressure above 130 Pa, the PSPs would be very useful for measurement in the low-pressure conditions. The result implies that the PSPs can be applied to microsystems.

(2) We have clarified that the PSP has distinct dependence of the luminescence intensity on the temperature. Because the dependence is comparable to that on the oxygen pressure, the temperature dependence should be considered when the pressure is deduced from the luminescence intensity, especially for applications in the low-pressure conditions.

(3) Pressure distributions on solid surfaces interacting with rarefied jets have been obtained using PdOEP bound by poly(TMSP), demonstrating the applicability of the PSP to the low-pressure conditions with the spatial resolution of 18 μm.

(4) We have discussed the dependence of luminescence intensity of PSP on the molecular number flux onto the solid surface. Because molecular number flux is an important quantity to analyze the interaction between high Knudsen number flows and solid surfaces, the PSP technique would become a powerful tool to measure molecular number flux in high Knudsen number regime.

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