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Application of Pressure-Sensitive Paints to Low-Pressure Range

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The pressure-sensitive paint (PSP) technique has potential as a powerful diagnostic tool for measurements in the high Knudsen number regime because it is based on luminescence of molecules. Three types of PSP [two composed of organic dye and polymer (luminophore/binder), platinum octaethylporphyrin (PtOEP)/silicone polymer (GP197) and platinumtetrakis (pentafluorophenyl) porphyrin (PtTFPP)/poly[1-(trimethylsilyl)-propyne] [poly(TMSP)], and the other ruthenium II tris (4,7-diphenyl-1, 10-phenanthrolin chloride (Bath-Ru) adsorbed on anodized aluminum] are applied to the rarefied gas flow mainly lower than 150 Pa (about 1 torr) to examine fundamental properties, such as pressure/temperature sensitivity, time response of luminescence, and so on. The results show PtTFPP/poly(TMSP) to be the most suitable PSP among them for application in the low-pressure range because it has very high and linear sensitivity against oxygen pressure. However, temperature sensitivity of PtTFPP/poly(TMSP) is not negligible, and a correction of temperature is required for quantitative pressure measurement with high accuracy. Finally, pressure distribution of a surface on which a low-density supersonic freejet impinges is measured by the PSP.

Nomenclature

A_n = Stern–Volmer coefficients
C = constant
D_Q = diffusion coefficient of oxygen molecules
E_A = Arrhenius activation energy
E_Q = activation energy related to the diffusion of oxygen molecules in the polymer
I = luminescence intensity of pressure-sensitive paint (PSP)
I_a = absorption intensity of PSP
I_{ref} = luminescence intensity of PSP at the known reference pressure P_{ref}
I_0 = luminescence intensity of PSP in the absence of oxygen
K = constant proportional to $K_Q + \tau_0$
K_Q = rate constant for oxygen quenching
k_0 = temperature-independent term of k_D
k_1 = temperature-dependent term of k_D
k_D = rate constant for radiationless deactivation
k_L = rate constant for luminescence
N = order of Stern–Volmer polynomial
N_m = number of molecules per millimole
$[O_2]$ = concentration of oxygen
P = total pressure
P_B = background pressure
P_{O2} = partial pressure of oxygen
P_{ref} = reference pressure
p = factor that depends on the quenching mechanism (in the Smoluchowski relation)
R_0 = universal gas constant
T = temperature
t = time
τ = lifetime of an excited luminescent molecule
Φ = luminescence quantum yield

Introduction

EXPERIMENTAL analyses of thermofluid phenomena with high Knudsen numbers, related to low-density gas flows or nanotechnologies, need measurement techniques based on atoms or molecules, for example, utilizing emission and absorption of photons, but the techniques lag in development compared with molecular simulation techniques. Several measurement techniques based on the interaction of laser beams with molecules have been proposed to clarify flowfield structures of low-density gas flows, phenomena of the temperature nonequilibrium, and so on. However, techniques for pressure measurement on solid surfaces in the low-pressure range have not been reported yet. In the case of gas flows in microsystems with a high Knudsen number, measurements of pressure on surfaces are rarely reported, and development of measurement techniques for such high Knudsen number regimes are eagerly anticipated. If pressure taps are used for measurement of pressure on solid surfaces placed in low-density gas flows, we cannot measure pressure precisely because of the large conductance of the capillary tubes connected to the taps, nor is it realistic to apply pressure taps to microsystems. In this study, we use pressure sensitive paint (PSP),[1–3] the principle of which is based on oxygen quenching of luminescence emitted from the paint irradiated by UV light, to measure pressure on solid surfaces in the low-pressure range.

Recently, many studies related to pressure measurements on solid surfaces using PSP have been reported.[4–7] In those studies, pressure on a surface is deduced from the calibration curve, which is obtained a priori in the range of pressure larger than about 1 torr (133.3 Pa).

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Because luminescence intensity decreases with an increase in the partial pressure of oxygen gas and does not change significantly in low-pressure range, the PSP technique has been considered inadequate for application. It prevents PSP from being used in the low-pressure range. Because the fluctuation of sensitivity and aging are notable in the low-pressure range, however, it is very important to understand the fundamental properties of PSP in the low-pressure range to obtain highly accurate measurement of pressure over a wide range of pressures.

In this study, we select three types of PSP {platinum octaethyl porphyin (PtOEP)/silicon polymer (GP197), ruthenium II tris (4, 7-diphenyl-1, 10-phenanthrolin cloride (Bath-Ru)/anodized aluminum (AA), and platinum tetrakis (pentafluorophenyl) porphyrin (PtTFPP)/poly[1-(trimethyl sily 1)-propyne][poly(TMSP)]} and examine their fundamental properties, such as pressure sensitivity, temperature dependence of luminescence intensity, and response of luminescence intensity on pressure change in the range of pressure below 150 Pa (about 1 torr). Finally, pressure distribution on a solid surface against which a supersonic freejet impinges is measured by the PSP, and the feasibility of using PSP for quantitative measurement is examined.

Luminescence Properties of PSP

In the PSP technique, pressure can be measured by oxygen quenching of luminescence emitted from luminescent molecules irradiated by a UV light.[1–3] High-luminescence intensity corresponds to the low-pressure region and low intensity to the high-pressure region. Pressure on the solid surface can be deduced from the relationship between the pressure and the luminescence intensity (Stern–Volmer plot).

Stern–Volmer Equation

A luminescence quantum yield Φ of PSP is given by[3]

$$\Phi = I/I_a = k_L/(k_L + k_D + K_Q[\mathrm{O_2}]) = k_L\tau \tag{1}$$

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

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

The concentration $[\mathrm{O_2}]$, the partial pressure of oxygen P_{O2}, and the total pressure P follow the relation $[\mathrm{O_2}] \propto P_{\mathrm{O2}} \propto P$, according to Henry's law. Because K_Q and τ_0 depend on the temperature T, Eq. (2) can be put in the form

$$I_0/I = 1 + K(T)P \tag{3}$$

Note that the constant K depends on the surface temperature T.

In practical applications 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

$$I_{\mathrm{ref}}/I = A_0(T) + A_1(T)(P/P_{\mathrm{ref}}) \tag{4}$$

The luminescence intensity I of the ideal PSP depends inversely on P as in Eq. (4), but the actual PSPs show nonlinearity of I on P. Therefore, the equation considering the nonlinearity is usually used as follows:

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

The Stern–Volmer coefficients A_n in Eqs. (4) and (5) are determined by the calibration tests. In practice, a second-order polynomial, $N = 2$, is commonly used.[3]

Temperature Dependence of Luminescence Intensity

Temperature dependence of the coefficients A_n in Eq. (5) is caused by that of k_L, k_D, and K_Q. The last two rate constants exert an influence on the luminescence intensity. The rate constant for radiationless deactivation k_D can be expressed by the sum of a temperature-independent term k_0 and a temperature-dependent term k_1, that is, $k_D = k_0 + k_1$. The rate constant k_1 is given by the Arrhenius equation, [3]

$$k_1 = C\exp(-E_A/R_0T) \tag{6}$$

Equation (6) states that k_1 increases as an increase in temperature T, so that k_D also increases, and as evidenced by Eq. (1), the luminescence intensity I decreases as T increases.

If polymer is used as a binder, the rate constant for oxygen quenching K_Q is usually dominated by the diffusion coefficient of the oxygen molecules in the polymer layer, which depends strongly on T. The K_Q is given by the Smoluchowski relation (see Ref. 3),

$$K_Q = 4\pi N_m p D_Q \tag{7}$$

The dependence of the diffusion coefficient D_Q of the oxygen molecules on T is also given by the Arrhenius equation, [3]

$$D_Q \propto \exp(-E_Q/R_0T) \tag{8}$$

D_Q increases as an increase in temperature T, which leads to an increase of $K_Q$as shown in Eq. (7). Therefore, it is clear from Eq. (1) that the luminescence intensity I decreases as an increase in temperature T. The diffusion coefficient D_Q depends also on the kind of the polymer, and the larger D_Q is, the higher the pressure sensitivity of PSP is and the more useful the binder with large D_Q becomes, especially for applications of PSP to rarefied gas flows.

PSP Descriptions

To select the PSP suitable for low-pressure conditions, fundamental properties of three types of PSPs (luminophore/binder) are examined in this study. Two of them are composed of organic dyes and polymers (luminophore/binder) PtOEP/GP197 and PtTFPP/poly(TMSP), and the other one is Bath-Ru adsorbed on an AA surface developed by Asai et al.[5]

PtOEP/GP197

This PSP employs PtOEP as a luminophore and GP197 as a binder. They are dissolved in an organic solvent and then painted on a base plate (substrate) by the use of an airbrush. PtOEP/GP197 is one of the first-generation PSPs[1] and has been widely used.

Bath-Ru/AA

Bath-Ru/AA is prepared by dipping an anodized sample made of aluminum into a solution of Bath-Ru in an organic solvent. Bath-Ru is adsorbed physically on the anodized porous surface. Because, in the case of Bath-Ru/AA, luminescent molecules are adsorbed on a base plate without a binder such as a polymer, it has been reported that this paint has fast response time and high sensitivity even in a cryogenic conditions.[4,5] However, it can be applied only to aluminum or aluminum alloys. Moreover, the binder limits the kind of luminophore. Ruthenium complexes such as Bath-Ru can be adsorbed on the AA surface, but many porphyrins cannot be adsorbed. TCPP and its complexes such as PtTCPP can be adsorbed on the AA surface, but it cannot be applied in the low-pressure regime because of its low sensitivity vs oxygen pressure.

PtTFPP/Poly(TMSP)

This paint employs PtTFPP as a luminophore and poly(TMSP) as a binder, both of which are dissolved by an organic solvent and then painted on a surface by an airbrush. PtTFPP has higher quenching performance for oxygen molecules and lower degradation by irradiation of light, compared to PtOEP. Poly(TMSP) is a polymer binder that is highly soluble in organic solvents such as toluene, and it can be combined with many kinds of porphyrins, which are also

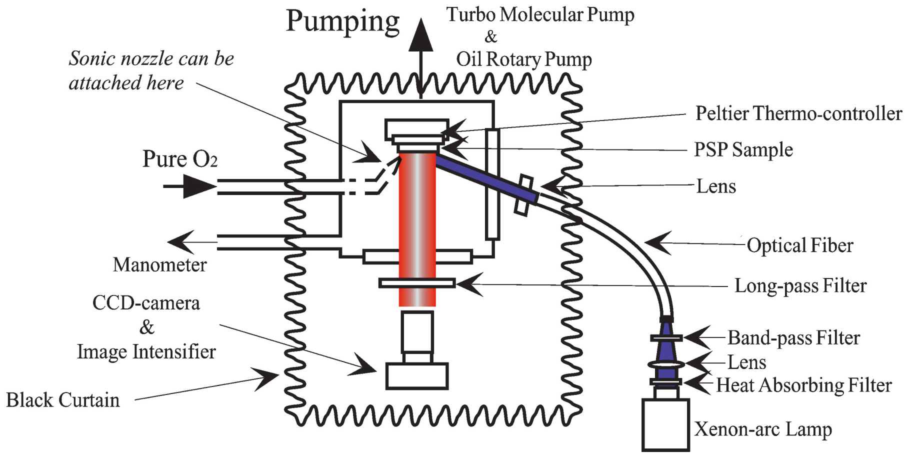


Fig. 1 Experimental apparatus.

highly soluble in organic solvents. Because poly(TMSP) is a glassy polymer with extremely high oxygen permeability,[5,7] it is expected that PtTFPP/poly(TMSP) has high-pressure sensitivity even in rarefied gas flow. Moreover, PtTFPP/poly(TMSP) can be applied to any materials, unlike Bath-Ru/AA.

Experimental Apparatus

Figure 1 shows the experimental apparatus for this study. The PSPs are painted on aluminum plates ($50 \times 25 \times 1$ mm^3). The samples of Bath-Ru/AA were prepared in accordance with Sakaue's procedure.[8] The current strength for anodization was fixed at 10 mA/cm^2 for every sample of Bath-Ru/AA. To prepare PtTFPP/poly(TMSP), 0.6 mg of PtTFPP and 40 mg of poly(TMSP) were dissolved in 5 cm^3 of toluene. The samples are set inside a vacuum chamber evacuated by a rotary pump (ULVAC, Inc. D-950) or a turbomolecular pump (ULVAC, Inc. UTM-300). Pure oxygen gas is supplied into the chamber where pressure is kept at 1.0×10^{-2}–151 Pa. Note that a converging nozzle can be attached at the supply port of the oxygen gas to carry out the experiments for a supersonic freejet impinging on the solid surface using the same vacuum chamber. The pressure is monitored by a capacitance manometer (ULVAC, Inc. CCMT-10A) and an ionization vacuum gauge (ULVAC, Inc. GI-1000). Using a Peltier thermocontroller and a thermocouple, the temperature of the PSP sample is kept at 293 K for PtOEP/GP197 and controlled in the range from 300 to 305 K for Bath-Ru/AA and PtTFPP/poly(TMSP). A xenon-arc lamp (Ushio UXL-500SX) with a bandpass filter is used as an excitation light source, and the light is transmitted via an optical fiber to illuminate the sample in the vacuum chamber. The wavelength ranges of the bandpass filters are 380 ± 20 nm for PtOEP/GP197, 450 ± 10 nm for Bath-Ru/AA, and 400 ± 10 nm for PtTFPP/poly(TMSP), which covers the absorption spectrum of each luminophore. The luminescence is filtered by a long-pass filter (600 nm) to eliminate the light from the xenon lamp and is detected by a charge-coupled devise (CCD) camera (Hamamatsu, C7300-10) with an image intensifier (Hamamatsu, C6653). The optical system including the vacuum chamber and CCD camera is covered with a black curtain to shut out stray light from outside the system. The luminescence image is processed by use of a personal computer, and the luminescence intensity is averaged over 200×200 pixels of the CCD camera.

Results and Discussion

Stern–Volmer Plots of the PSPs

Figure 2 shows the Stern–Volmer plots for PtOEP/GP197, Bath-Ru/AA, and PtTFPP/poly(TMSP) at pressure below 150 Pa. The horizontal axis is the pressure on the sample surface, and the vertical axis is the relative luminescence intensity (I_{ref}/I) in Eqs. (4) and (5). The surface temperature of each sample is kept at 300 K (at 293 K for PtOEP/GP197). The pressure ranges are 1.0×10^{-2}–151 Pa for PtOEP/GP197, 1.0×10^{-2}–152.5 Pa for Bath-Ru/AA, 2.7-153.6 Pa for PtTFPP/poly(TMSP). The reference pressure P_{ref} of each datum is set at the lower limit of the pressure range.

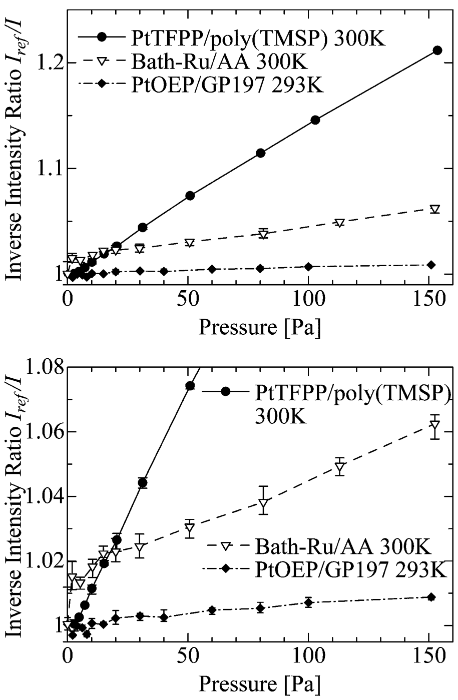


Fig. 2 Stern–Volmer plots for PtOEP/GP197, BathRu/AA, and PtTFPP/poly(TMSP).

It is clearly seen from Fig. 2 that the luminescence intensity of PtOEP/GP197 hardly changes in the range of pressure below 150 Pa, and it has little pressure sensitivity deduced from the slope of the Stern–Volmer plot. The result is attributed to insufficient gas permeability of the polymer GP197 used as the binder, so that oxygen molecules almost never diffuse into the binder and quench the luminescence of PtOEP. This result indicates that PtOEP/GP197 is not suitable for pressure measurement in the low-pressure range below 150 Pa.

The inverse luminescence intensity ratio I_{ref}/I for Bath-Ru/AA depends linearly on the pressure ratio P/P_{ref} at the pressure above 20 Pa, but nonlinear dependence appears below 20 Pa. The nonlinearity is probably caused by adsorption of oxygen molecules on the AA surface. The relatively high-pressure sensitivity of Bath-Ru/AA even in low-pressure conditions seems to be due to the quenching mechanism, namely, that the Bath-Ru molecules adsorbed on the anodized surface interact directly with oxygen molecules. On the other hand, the nonlinear dependence makes the calibration of Bath-Ru/AA difficult.

PtTFPP/poly(TMSP) shows the highest pressure sensitivity among the three types of PSPs examined in this study and good linearity of the Stern–Volmer plot over the entire pressure range. Also note that the absolute luminescence intensity of PtTFPP/poly(TMSP) is the highest among the three types of PSPs and results in the highest signal-to-noise ratio (S/N). We consider that such properties are due to large free volume [9] of poly(TMSP), unlike GP197, so that oxygen molecules can permeate more easily through polymer matrix.

In the followings sections we examine indetail the properties of Bath-Ru/AA and PtTFPP/poly(TMSP) that have sufficient pressure sensitivity in the low-pressure range mentioned earlier.

Properties of Bath-Ru/AA at Very Low Pressure

As mentioned, Bath-Ru/AA shows nonlinearity in the Stern–Volmer plot at pressure below 20 Pa. This seems to be due to the adsorption of oxygen molecules to the anodized oxide layer, and it is related to the amount of the adsorption of the luminescent molecules. To clarify the effect of the adsorption of oxygen molecules in the low pressure range, we examine and compare the luminescence properties for four types of samples on which different amount of Bath-Ru is deposited.

The thickness of the anodized oxide layer can be controlled by changing the anodizing time; the longer the anodizing time, the thicker the layer becomes. The amount of Bath-Ru deposited on AA can be controlled by changing the dipping time in a Bath-Ru solution. In this paper, each sample is specified as anodizing time (minutes)–dipping time (seconds). For example, 5–10 indicates the sample whose anodizing time is 5 min and dipping time is 10 s. The Bath-Ru/AA sample examined in the preceding section is 15–10. In this section, four Bath-Ru/AA samples (5–1, 15–1, 5–10, and 15–10) are examined, and the dependence of the properties on their anodizing time and dipping time are discussed.

Comparison of Stern–Volmer Plots

The Stern–Volmer plots for the four Bath-Ru/AA samples with surface temperature of 300 K are shown in Fig. 3. The pressure ranges are 4.5×10^{-2}–133.6 Pa for 5–1 and 15–1 samples, 4.0×10^{-2}–137.3 Pa for 5–10 sample, and 1.0×10^{-2} –152.5 Pa for 15–10 sample. In Fig. 3, the vertical axis indicates the relative luminescence intensity (I_{ref}/I) and the horizontal axis the absolute pressure. The reference intensity I_{ref} is obtained at the minimum of the pressure range for each PSP.

Samples of 5–1 and 15–1 with small amounts of luminescent molecules show the linearity of the Stern–Volmer plots even in the range of pressure above 10 Pa. However, the plot for 15–10 sample shows the strong nonlinearity below 20 Pa, as shown in the preceding section. Collision of the oxygen molecules with the luminescent molecules contacting directly with the ambient gas dominates the quenching in the 5–1 and 15–1 cases In addition, it seems that the diffusion and the adsorption of the oxygen molecules into the pores have significant effect on the quenching in the 15–10 case, which shows nonlinearity of the Stern Volmer plot.

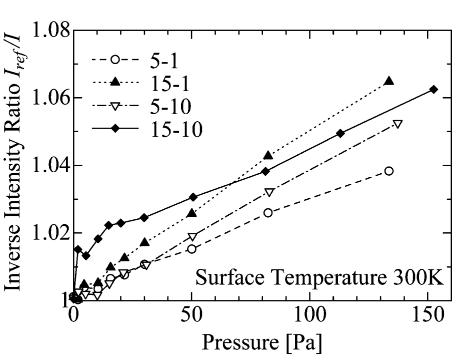
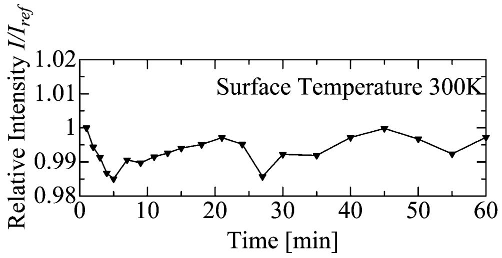
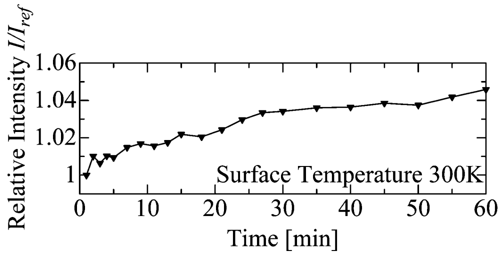


Fig. 3 Stern–Volmer plots for Bath-Ru/AA, 5–1, 15–1, 5–10 and 15–10 samples.



a) 1.1×10^{-2} Pa → 133 Pa



b) 133 Pa → 1.2×10^{-2} Pa

Fig. 4 Luminescence intensity of Bath-Ru/AA with 5–10 sample for abrupt change of pressure at 300 K.

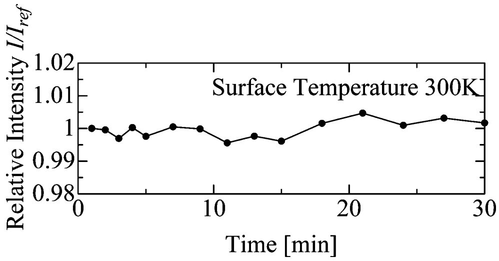
In Fig. 3, the 15–1 sample has the highest pressure-sensitivity in the range of pressure below 150 Pa; however, note that the smaller the amount of the luminescent molecules, the weaker the luminescence intensity, which leads to low S/N in the pressure measurement.

Change of Luminescence Intensity for Abrupt Change of Pressure (Effect of Adsorption of Oxygen Molecules)

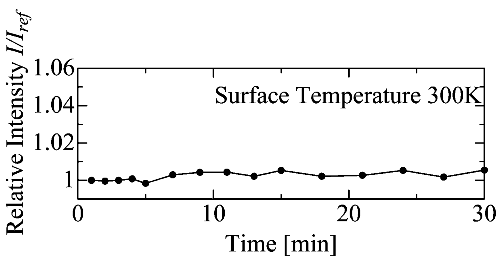
To clarify how the diffusion and the adsorption of oxygen molecules exert influence on the luminescence intensity of Bath-Ru/AA, its temporal responses for abrupt change of pressure are examined for the four samples of Bath-Ru/AA.

Figure 4a shows the temporal response of the luminescence intensity I for the 5–10 sample after the pressure in the chamber was kept at 1.1×10^{-2} Pa for 1 h and then increased abruptly to 133 Pa. Figure 4b, on the contrary, shows the temporal response after the pressure in the chamber was kept at 133 Pa and then decreased abruptly to 1.2×10^{-2} Pa. During the experiments, the temperature T of the sample is kept at 300 K. The same experiments were also carried out for the 5–1, 15–10, and 15–1 samples, and the results are shown in Fig. 5, 6, and 7, respectively. In Figs. 4–7, the horizontal axis indicates the time (minutes) and the time $t = 0$ is defined as the instant when the pressure in the chamber reached the desired value (133 Pa for Fig. 4a and 1.2×10^{-2} Pa for Fig. 4b). The measurements of luminescence intensity were started 1 min later. Therefore, the start time of the measurement corresponds to about 2 min after the onset of the pressure change because the arrival time to the desired pressure is about 1 min. In Figs. 4–7, note that the vertical axis is not the inverse intensity ratio I_{ref}/I but I/I_{ref} and I_{ref} means the initial luminescence intensity at $t = 1$ min. (Unlike the Stern–Volmer plot, I_{ref} is not the intensity at the reference pressure, so that I/I_{ref} is proportional to the absolute luminescence intensity.)

The luminescence intensity I of the 5–10 sample with large adsorption amount of Bath-Ru decreased monotonously during the first several minutes after the abrupt increase of pressure as shown in Fig. 4a. This is because most of oxygen molecules adsorbed inside the pores of the anodized oxide layer are desorbed for about 1 h when the sample is left in the chamber kept at 1.1×10^{-2} Pa and, after abrupt increase of the pressure, oxygen molecules diffuse gradually into the pores and quench the luminescence. The 15–10 sample also showed the same tendency as the 5–10 sample, as shown in Fig. 6. On the other hand, the luminescence intensity of the 5–1 sample (and 15–1 sample) did not change against the abrupt change in the pressure, as shown in Fig. 5 and 7. We can conclude that the larger the amount of the adsorbed luminescent molecules, that is, the longer dipping time, is the stronger the influence of the diffusion

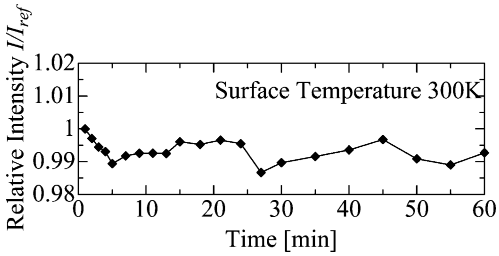


a) 1.1 × 10^{-2} Pa → 133 Pa

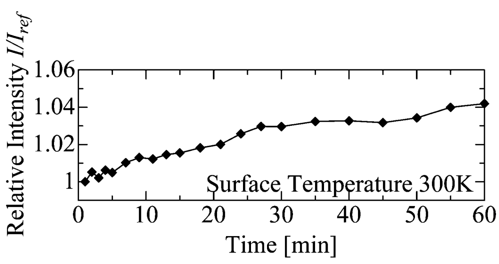


b) 133 Pa → 1.2 × 10^{-2} Pa

Fig. 5 Luminescence intensity of Bath-Ru/AA with 5–1 sample for abrupt change of pressure at 300 K.



a) 1.1 × 10^{-2} Pa → 133 Pa

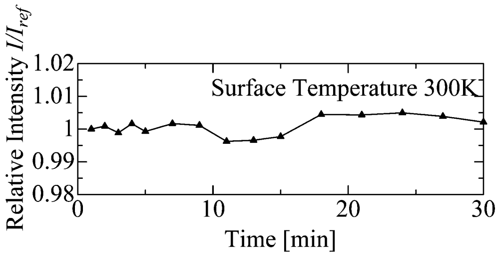


b) 133 Pa → 1.2 × 10^{-2} Pa

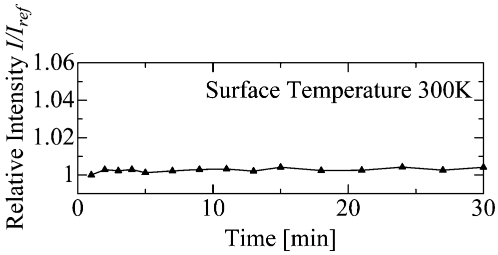
Fig. 6 Luminescence intensity of Bath-Ru/AA with 15–10 sample for abrupt change of pressure at 300 K.

of oxygen molecules on the temporal response of the luminescence intensity becomes.

When the pressure was decreased abruptly, the luminescence intensity I of the 5–10 and 5–1 samples increased monotonously long after 1 h, as shown in Figs. 4b and 5b. This may be because a large amount of oxygen molecules diffused into the pores of the anodized oxide layer for 1 h when the sample was left in the chamber kept at 133 Pa, and after the abrupt decrease of pressure, the oxygen molecules were desorbed gradually from the pores and increased the luminescence.



a) 1.1 × 10^{-2} Pa → 133 Pa



b) 133 Pa → 1.2 × 10^{-2} Pa

Fig. 7 Luminescence intensity of Bath-Ru/AA with 15–1 sample for abrupt change of pressure at 300 K.

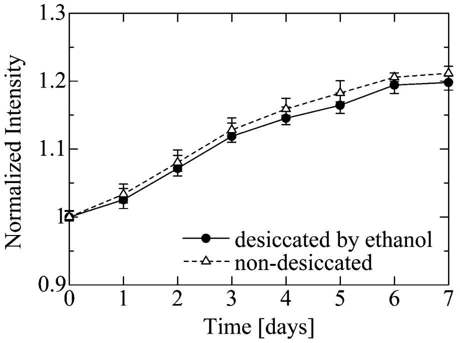
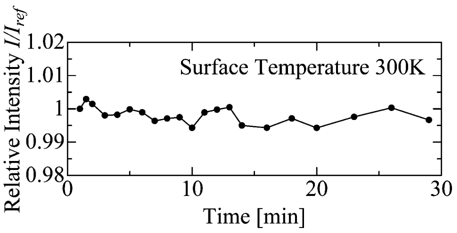


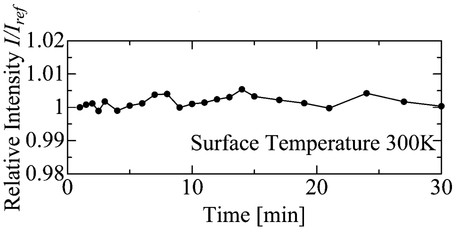
Fig. 8 Aging of luminescence intensity of Bath-Ru/AA, 15–10 sample.

On the other hand, it is reported that water molecules can quench the luminescence of PSPs.[2] Because the aluminum surface was anodized in dilute sulfuric acid solution, water molecules might be adsorbed on the surface. In that case, it might be considered that the adsorbed water molecules were desorbed very slowly as time passes. Because the desorption of oxygen molecules from the pores of the anodized oxide layer usually takes long time to become saturated, variation of the luminescence intensity of Bath-Ru is examined over several days, with the 15–10 sample with large Bath-Ru adsorption amount set in the chamber kept at low pressure. To examine the quenching effect of water molecules, the result of a sample desiccated by absolute ethanol was compared with that of a nondesiccated sample. In the experiment, two 15–10 samples were prepared. One sample was desiccated by dipping in absolute ethanol for 15 min before the sample was dipped into the Bath-Ru solution. The other was prepared without the desiccation. The two samples were tested simultaneously in the same pressure condition and the change of luminescence intensity, compared. Figure 8 shows the result of the experiment carried out for 7 days, in which the luminescence intensity was measured every 24 h with the chamber pressure of 3.0×10^{-3} Pa and the surface temperature of the samples of 300 K. In Fig. 8, the luminescence intensity of each sample is normalized by that of the zeroth day (the day when the samples were placed into the chamber). It is found from Fig. 8 that the slope of the luminescence intensity is approximately linear for the first 3 days, but it become smaller after the 4 day and almost flat on the 7th day. There was very little difference between the desiccated sample and the nondesiccated one. Generally, the luminescence intensity decreases day by day due to the aging and degradation by irradiation of light, but the results of Fig. 8 show the opposite tendency.

Therefore, it is considered from the results of Figs. 4–8 that the desorption of oxygen molecules inside the pores of the anodized oxide layer mainly causes a gradual increase in the luminescence intensity. Because it takes about one week for samples with large adsorption amount of Bath-Ru, that is, with long dipping time, to desorb oxygen molecules inside the pores, care should be taken to use Bath-Ru/AA for measurement of pressure on a solid surface whether the pressure change abruptly or not.

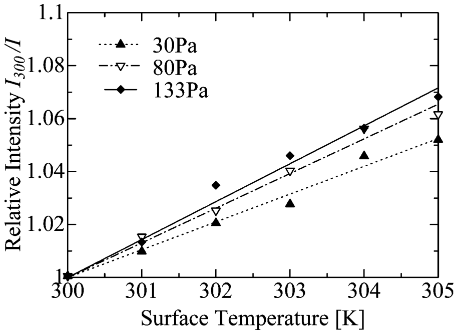


a) 2.7 × 10^{-3} Pa → 133 Pa

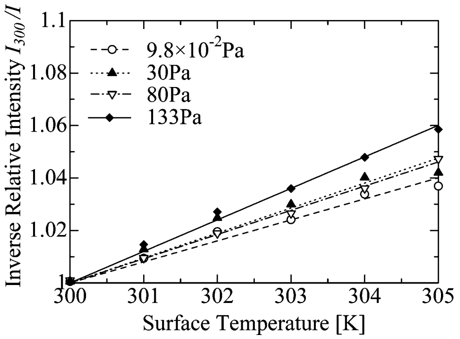


b) 133 Pa → 3.4 × 10^{-3} Pa

Fig. 9 Luminescence intensity of PtTFPP/poly(TMSP) for abrupt change of pressure.



a) Bath-Ru/AA(5-10)



b) PtTFPP/poly (TMSP)

Fig. 10 Temperature dependence of PSPs for various pressures.

On the other hand, Bath-Ru/AA with a small amount of Bath-Ru, that is, with short dipping time, is less affected by the diffusion of oxygen molecules on the anodized oxide layer, as shown in Fig. 5. However we must emphasize that its absolute luminescence intensity is relatively small, leading to low S/N. It is concluded, as mentioned earlier that Bath-Ru/AA cannot be applied for the quantitative and precise measurement of surface pressure in the low-pressure conditions.

Properties of PtTFPP/poly(TMSP) at Very Low Pressure

The properties of PtTFPP/poly(TMSP), one of the polymer-based PSPs, is examined in the low-pressure range and compared with Bath-Ru/AA.

Change of Luminescence Intensity for Abrupt Change of Pressure

To examine the effect of the desorption and the diffusion of oxygen molecules on the luminescence intensity of PtTFPP/poly(TMSP), the same experiments as described in the preceding section were carried out for PtTFPP/poly(TMSP). Figure 9a shows the temporal response of the luminescence intensity I of PtTFPP/poly(TMSP) after the pressure in the chamber was kept at 2.7×10^{-3} Pa for 1 h and then increased abruptly to 133 Pa. Figure 9b shows the temporal response for the same sample after the pressure in the chamber was kept at 133 Pa and then decreased abruptly to 3.4×10^{-3} Pa. Measurement time was 30 min for both experiments, and the temperature T of the sample was kept at 300 K.

It is found from Figs. 9a and 9b that PtTFPP/poly(TMSP) showed no distinct increase or decrease in the luminescence intensity as shown in Figs. 4a and 4b for Bath-Ru/AA. This may be because the luminescent molecules do not contact directly with the ambient gas, but are protected by poly(TMSP), glassy polymer with high oxygen permeability. Moreover, the fluctuation of the luminescence intensity of PtTFPP/poly(TMSP) remained within ±0.5%.

Other Properties of PtTFPP/poly(TMSP)

We carried out the experiments for iterations of pressurization and depressurization for PtTFPP/poly(TMSP) and found that the Stern–Volmer plot did not fluctuate. It is also clear from these results that PtTFPP/poly(TMSP) is less affected by the diffusion of oxygen molecules into the polymer. In addition, the absolute luminescence intensity of PtTFPP/poly(TMSP) was the highest among the three types of PSPs, leading to the pressure measurement with high S/N.

Luminescence Intensity Dependence on Temperature for Bath-Ru/AA and PtTFPP/poly(TMSP) at Very Low Pressure

Because the luminescence intensity of PSPs depends not only on partial pressure of oxygen gas but also temperature, fluctuation of temperature causes an error in pressure measurements. In this section, we describe the temperature dependence of the luminescence intensity of Bath-Ru/AA and PtTFPP/poly(TMSP).

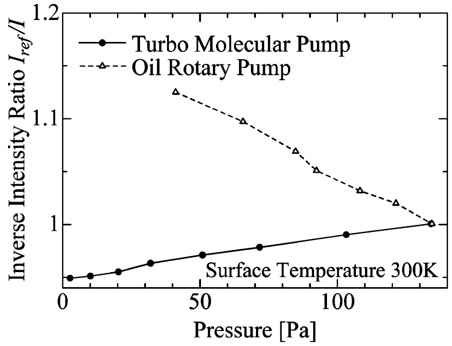
The dependence of the luminescence intensity on the surface temperature of the PSP samples was measured by changing the surface temperature of the PSP sample in the range of 300–305 K with 1-K steps, for the oxygen pressure of 9.8×10^{-2}, 30, 80, and 133 Pa. Note that the chamber was kept at each pressure for a long time after the samples of Bath-Ru/AA were placed inside it, to eliminate the effect of the diffusion of the oxygen molecules into the pores of the anodized aluminum layer.

Figure 10 shows the temperature dependence of the luminescence intensity of Bath-Ru/AA and PtTFPP/poly(TMSP) for several pressure conditions. In Fig. 10, the vertical axis is the relative luminescence intensity (I_{300}/I) normalized by I_{300} at 300 K at each pressure, and the horizontal axis is the surface temperature. The curves in Fig. 10 are obtained by the method of least squares to pass through both points at 300 K and $I_{300}/I = 1$. In Fig. 10a, only the result for 5–10 sample is shown, but we also carried out the same experiments for the four samples of Bath-Ru/AA. All of the samples of Bath-Ru/AA showed the same tendency of temperature dependence.

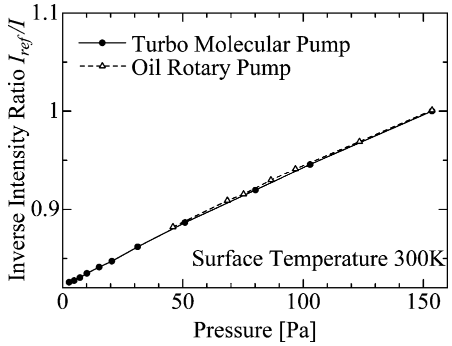
The results shown in Fig. 10 indicate that the luminescence intensity decreases as temperature increases and that the higher the pressure, the larger the temperature sensitivity, that is, the slope. This is because k_1 and D_Q [and consequently k_D and k_Q given by Eq. (6) and (7), respectively] increase with an increase in temperature, which leads to a decrease in the luminescence intensity. It is also found from Fig. 10 that the higher the pressure the larger the rate of decrease in the luminescence intensity. It seems that this result is caused by the rate constant k_Q [Eq. (1)], which depends complicatedly on both the oxygen pressure and the surface temperature. Because the temperature dependence of the luminescence intensity is not negligibly small as evidenced in Fig. 10, we consider that correction for the surface temperature is required absolutely for precise pressure measurements using PSP.

Influence of Pump Oil Vapor on Pressure Sensitivity for Bath-Ru/AA

Figure 11 shows a difference between the Stern–Volmer plots of Bath-Ru/AA and PtTFPP/poly(TMSP) depending on whether



a) Bath-Ru/AA



b) PtTFPP/poly (TMSP)

Fig. 11 Stern–Volmer plots with use of an oil-rotary pump and a turbomolecular pump.

an oil-rotary pump or a turbomolecular pump is used to evacuate the chamber. In Fig. 11, I_{ref} is the luminescence intensity at $P_{\text{ref}} = 134.1$ Pa. The Stern–Volmer plot for the oil-rotary pump is shown by a solid line and that for the turbomolecular pump by a broken line. As clearly seen from Fig. 11a, both plots of Bath-Ru/AA change inversely, that is, the higher the pressure, the brighter the luminescence when evacuated by the oil-rotary pump, that is, negative slope, contrary to the normal property of the PSP. This may be due to oil vapor in the chamber, which emitted from the oil-rotary pump. Because, in the case of Bath-Ru/AA the luminescent molecules are adsorbed directly on the anodized surface and the surface is formed by a large number of the pores (large surface area), the oil vapor easily interacts with the luminescent molecules and easily adsorbs on the surface, which rapidly changes the property of the PSP. On the other hand, as shown in Fig. 11b, there is no significant difference between the Stern–Volmer plots of PtTFPP/poly(TMSP) for evacuation by the oil-rotary and by the turbomolecular pump, unlike Bath-Ru/AA. We consider this result to be because the luminescent molecules are protected by the poly(TMSP) layer against the contamination by the pump oil and are not exposed directly to the atmosphere.

Measurement of Pressure Distribution on a Solid Surface Interacting with a Supersonic Freejet

As an application of PSP to low-density gas flows, we measured the pressure distribution of a solid surface interacting with a supersonic freejet. When the preceding results were considered, PtTFPP/poly(TMSP) was adopted as the PSP for the experiment because it is less affected by the diffusion of oxygen molecules into the polymer. In the experiment, a converging nozzle was attached at the supply port of oxygen gas and the temperature of the solid surface is kept at 300 K.

Figure 12 is the Stern–Volmer plot of PtTFPP/poly(TMSP) at 300 K in the pressure range of 9.3 Pa–3.6 kPa, which is used for the calibration. The reference luminescence intensity I_{ref} was measured at $P_{\text{ref}} = 132.8$ Pa. The solid line was given by the least-square fitting with the second-order Stern–Volmer equation (5) with $N = 2$ and the Stern–Volmer coefficients A_n were deduced as $A_0 = 9.03 \times 10^{-1}$, $A_1 = 9.41 \times 10^{-2}$, and $A_2 = -7.97 \times 10^{-4}$.

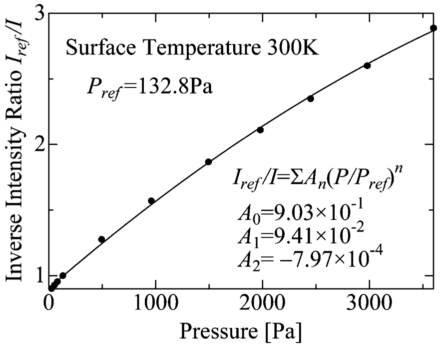


Fig. 12 Stern–Volmer plot in the wide pressure range for PtTFPP/poly(TMSP).

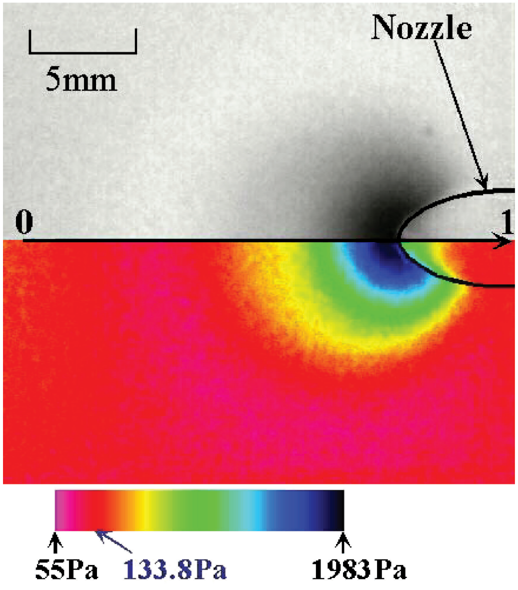


Fig. 13 Pressure distribution and pseudocolor on solid surface interacting with an impinging supersonic freejet using PtTFPP/poly(TMSP).

The upper part of Fig. 13 shows the output of the CCD camera imaging the solid surface on which a supersonic freejet impinges, and the lower part the pseudocolor image of the pressure distribution estimated from the Stern–Volmer plot shown in Fig. 12. In Fig. 13, the source pressure of the jet and the background pressure in the chamber are set at 53.9 kPa and 133.8 Pa (pressure ratio = 403), respectively. The nozzle diameter is 0.3 mm, the impinging angle is 60 deg, and the distance from the nozzle exit to the surface is 2 mm. The distinct image of the pressure distribution could be obtained, as shown in Fig. 13, although we had not compensated for local fluctuation of the surface temperature caused by the jet impingement because the density of the jet is low.

In the same geometrical condition as Fig. 13, the luminescence intensity distributions were imaged for various background pressures P_B (133.8, 80.2, 50.9, and 31.2 Pa), and the surface pressure distributions along the projection line of the centerline of the impinging jet are estimated as shown in Fig. 14. The horizontal axis of Fig. 14 is the distance normalized by the whole length of the projection line shown in Fig. 13, and the origin is placed downstream. As shown in Fig. 14, the pressure far from the nozzle exit is close to the background pressure in every case. The obtained pressures downstream were 46.2 ± 8.0, 72.4 ± 7.7, 120.0 ± 7.2, and 196.0 ± 13.2 Pa for $P_B = 31.2$, 50.9, 80.2, and 133.8 Pa, respectively. The results indicate the possibility of quantitative measurement technique of the surface pressure using PtTFPP/poly(TMSP) even in the low-pressure range. To accomplish quantitative pressure measurements with high accuracy, however, simultaneous measurement of surface

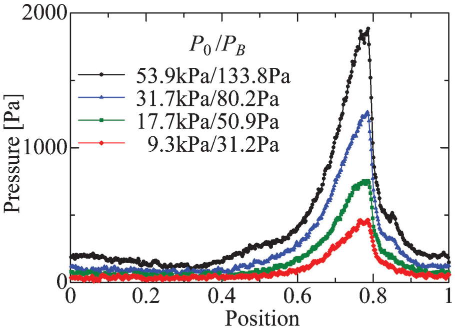


Fig. 14 Pressure distribution along a centerline of a solid surface interacting with an impinging supersonic freejet using PtTFPP/poly(TMSP).

temperature is necessary to compensate for the dependence of luminescence intensity of PSP on the temperature.

We have also tried to measure the pressure distribution on the surface using Bath-Ru/AA, but the pressure measured far from the nozzle exit did not coincide with the background pressure quantitatively, although qualitative pressure distribution map could be obtained. The obtained pressures downstream were 249.6 ± 98.6, 260.3 ± 83.3, 393.4 ± 185.6, and 658.0 ± 218.8 Pa for $P_B = 31.5$, 51.5, 80.5, and 133.6 Pa, respectively, all of which are more than four times as large as the background pressures P_B with large uncertainty more than 160% of P_B. Therefore, we have concluded that it is impossible to measure quantitative pressure distributions on solid surfaces by Bath-Ru/AA in the low-pressure region.

Summary

In this study, we have examined the fundamental properties of three types of PSPs [PtOEP/GP197, Bath-Ru/AA, and PtTFPP/poly(TMSP)] in low-pressure conditions below 150 Pa (about 1 torr), which had not been clarified yet, to clarify the feasibility of PSP for measurement of surface pressure in high Knudsen number flows. The following conclusions were reached:

1) PtOEP/GP197, which is a first-generation PSPs, has little pressure sensitivity as deduced from the slope of the Stern–Volmer plot in the range of pressure below 150 Pa, attributed to insufficient gas permeability of the polymer GP197 used as the binder.

2) Bath-Ru/AA with small amount of luminescent molecules demonstrates linearity in the Stern–Volmer plot even in the range of pressure above 10 Pa, but that with large amount of luminescent molecules, demonstrates strong nonlinearity below 20 Pa. From the viewpoint of low S/N in the former and the desorption of oxygen molecules inside the pores of the anodized oxide layer in the latter, Bath-Ru/AA could not be expected to measure the pressure distribution on solid surfaces quantitatively in the low-pressure range. Moreover, pump oil vapor significantly affects the Stern–Volmer plot of Bath-Ru/AA, which causes large errors in pressure measurements.

3) PtTFPP/poly(TMSP) has the highest luminescence intensity among the three types of PSPs and shows linear sensitivity in the low-pressure range. For iterations of pressurization and depressurization, the Stern–Volmer plot for PtTFPP/poly(TMSP) did not fluctuate. PtTFPP/poly(TMSP) with these features enables quantitative measurement of pressure.

4) The luminescence intensity decreases as temperature increases, and the higher the pressure, the larger the temperature sensitivity, that is, the slope. This is because the rate constants for quenching increase as an increase in temperature, which leads to a decrease in the luminescence intensity. It is also found that the higher the pressure the larger the rate of the decrease in the luminescence intensity. It seems that the dependence is caused by the rate constant k_Q, which depends complicatedly on both the oxygen pressure and the surface temperature. Because the temperature dependence of the luminescence intensity is not negligible, the correction for the surface temperature is necessary for precise pressure measurements using PSP.

5) Pressure distribution on a solid surface interacting with an impinging supersonic freejet has been measured using PSPs, showing the usefulness of PtTFPP/poly(TMSP) and the difficulty of Bath-Ru/AA for measurements of quantitative pressure distribution in the low-pressure range.

Acknowledgments

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